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TECHNICAL REPORT
TR 76-39-CEMEL

LIQUID-INJECTION-MOLDED, LIGHTWEIGHT, INSULATED FOOTWEAR

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December 1975

UNITED STATES ARMY
NATICK RESEARCH and DEVELOPMENT COMMAND
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Clothing, Equipment and Materials Engineering Laboratory

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The purpose of this work was to develop a suitable process for manufacturing lightweight, insulated footwear (LIF) on automated, liquid-injection-molding (LIM) equipment. Improvements in compounds, mold design and chemistry were incorporated into a completely new method for fabricating the LIF; this method, adaptable to automation, has the capability of molding a boot with a low-density upper and higher density outsole in one cycle. The improved molds compound formulations, processing equipment and techniques produced good quality LIF. Thirty pairs of LIF were made, and 25 were sent to Alaska for

20. ABSTRACT (cont'd)

testing.

PREFACE

The physical properties and thermal adequacy of the standard black insulated U. S. Army boot for cold-wet use have been validated by actual field experience. These properties were achieved at the expense of weight (each boot weighs 40-44 ounces). Studies of the energy consumption of the combat soldier indicate that one ounce of weight carried on the foot is equivalent to six ounces carried on the back, and therefore, two 40 ounce boots are equivalent to 30 pounds. In view of this, the development of a new concept for producing lightweight insulated footwear, while retaining other required physical properties, becomes essential. The boots should be in the weight range of 26 ounces per boot (size 9R), be durable and flexible, and offer environmental protection at temperatures as low as $-30^{o}C$.

This report describes the work performed during the 24-month period from 30 October 1973 to 30 September 1975 under continuation of a program previously initiated with Uniroyal, Incorporated. Under the supervision of Project Officer Joseph E. Assaf, U. S. Army Natick Development Center, the materials and processing techniques culminating in the production of lightweight polyurethane insulated footwear by the liquid injection molding process were performed by Uniroyal, Incorporated, Middlebury, Connecticut. The work was conducted under Project 1T762723AH98AA Energy Conservation through Lightweight Clothing and Equipment Systems under contract no. DAAK03-74-C-0027.

The Project Officer wishes to acknowledge the valued suggestions of Dr. Malcom C. Henry, Chief of the Materials Application Division of the Clothing Equipment and Materials Engineering Laboratory, and the guidance of Mr. Douglas S. Swain, Footwear Technologist at NDC relative to design considerations.

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INTRODUCTION

The main objectives of this contract were to optimize materials, conduct mold design studies, modify the previously developed chemistry, and develop a manufacturing process suitable for fabricating lightweight, insulated footwear (LIF) on automated, liquid-injection-molded (LIM) equipment and to fabricate 30 pairs of lightweight, insulated footwear by this process for evaluation by the Government.

The information developed under lightweight, insulated footwear contract (DAAG17-72-C-0058) dated November 3, 1971, including formulations, processing techniques and actual fabrication of prototype footwear was used as a guideline in the attainment of the required objectives. Experimental work was based upon the conclusions reached and trends established by the previous government contract work and continued from that point to establish the required product modifications and manufacturing process.

Development work in Phase I was concentrated in the following areas:

1. Boot Design Studies
2. Molds and Mold Holder
3. Liquid Injection Molding (LIM) Equipment
4. Adaptation of Developed Chemistry to LIM Equipment and Processing
5. Materials Optimization
6. Process Steps
7. Preparation of Prototype Samples

Phase II consisted of producing the specified 30 pair of lightweight insulated footwear as represented by the approved prototypes.

I. BOOT DESIGN STUDIES

After reviewing the results of the Alaskan wear test initiated in 1972 involving the cast LIF (Lightweight Insulated Footwear) boots fabricated during the previous government contract, several changes in boot design were made in an effort to improve boot performance.

A. All boots wear-tested in Alaska by the U. S. Army exhibited outer skin cracking in the vamp from one-half inch to five inches in length across the mold seal line. This flex crack area is indicated as Point #1 in Figure 1. To reduce skin cracking, the sharp curvature in the vamp area was changed to a more gradual radius. This contributes to a slight increase in thickness but should reduce the outer skin cracking by distributing the stress over the larger area. This design change is illustrated in Figure 2. The last dimension was not changed to compensate for any of the design changes.

B. Eighty percent of the boots wear-tested in Alaska had cracked outer skin following the outsole line in the heel and toe areas. Points #2 and #3 in Figure 1 indicate these areas. To reduce outer skin cracking in these areas an outsole wrap was extended around the outsole of the boot. This involves extending the higher density outsole foam further up the foxing area. The outsole wrap is outsole material as illustrated by Points #2 and #3 in Figure 2. The wrap will be at a level line around the boot and extend above the boot last line. This extension of outsole material should relieve stress on the joint line between the upper and outsole.

C. Chunking out of cleats in the forward shank area of the outsole was observed in forty percent of the boots worn in the Alaskan test, (Point #4, Figure 1). The last mid-cleat of the outsole was eliminated since the wear tests have shown that this cleat usually tears out.

D. Point #5 in Figure 1 illustrates the steep angle front heel used in the cast LIF boot. The sharpness of this angle was reduced and a more gradual radius was used on the breast of the heel as shown in Point #5 in Figure 2. This change distributes the stress along the heel mold line and thereby improves the flex life of the outsole.

E. To improve serviceability of the outsole, several outsole patterns were designed that could improve traction and flex crack resistance and reduce the chunking out and the abrasive wear of cleats. The outsole designs considered are shown in Figures 3 thru 7 as RT-1, RT-2, RT-3, RT-4 and JA-1. RT-1, RT-4 and JA-1 were chosen for further study, and metal outsole plates were made of these designs. Design RT-1 was used on the white colored Arctic Boot (contract

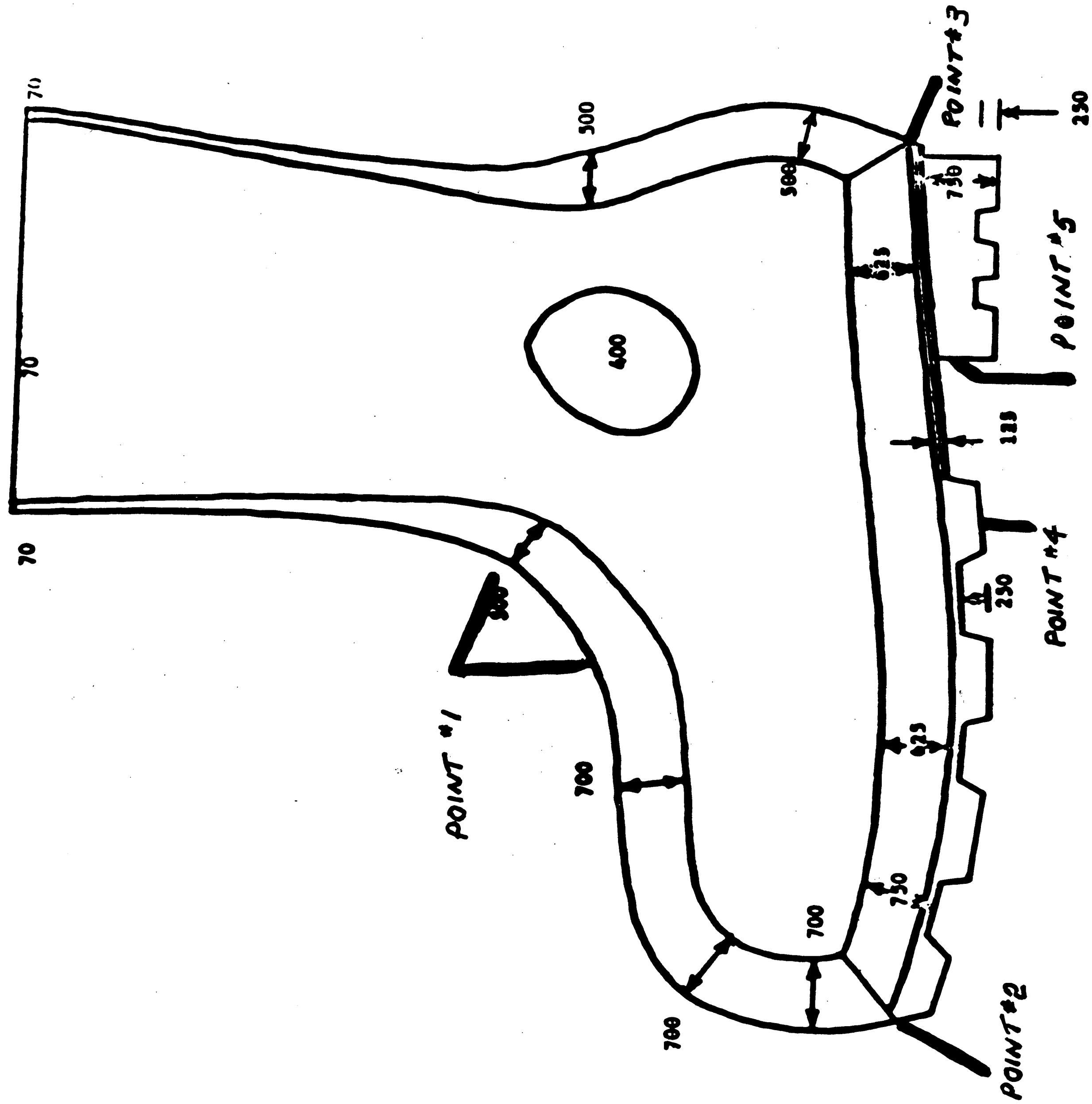

FIGURE 1
SCHEMATIC OF BOOT DESIGN
CONTRACT DAAG17-72-C-0058

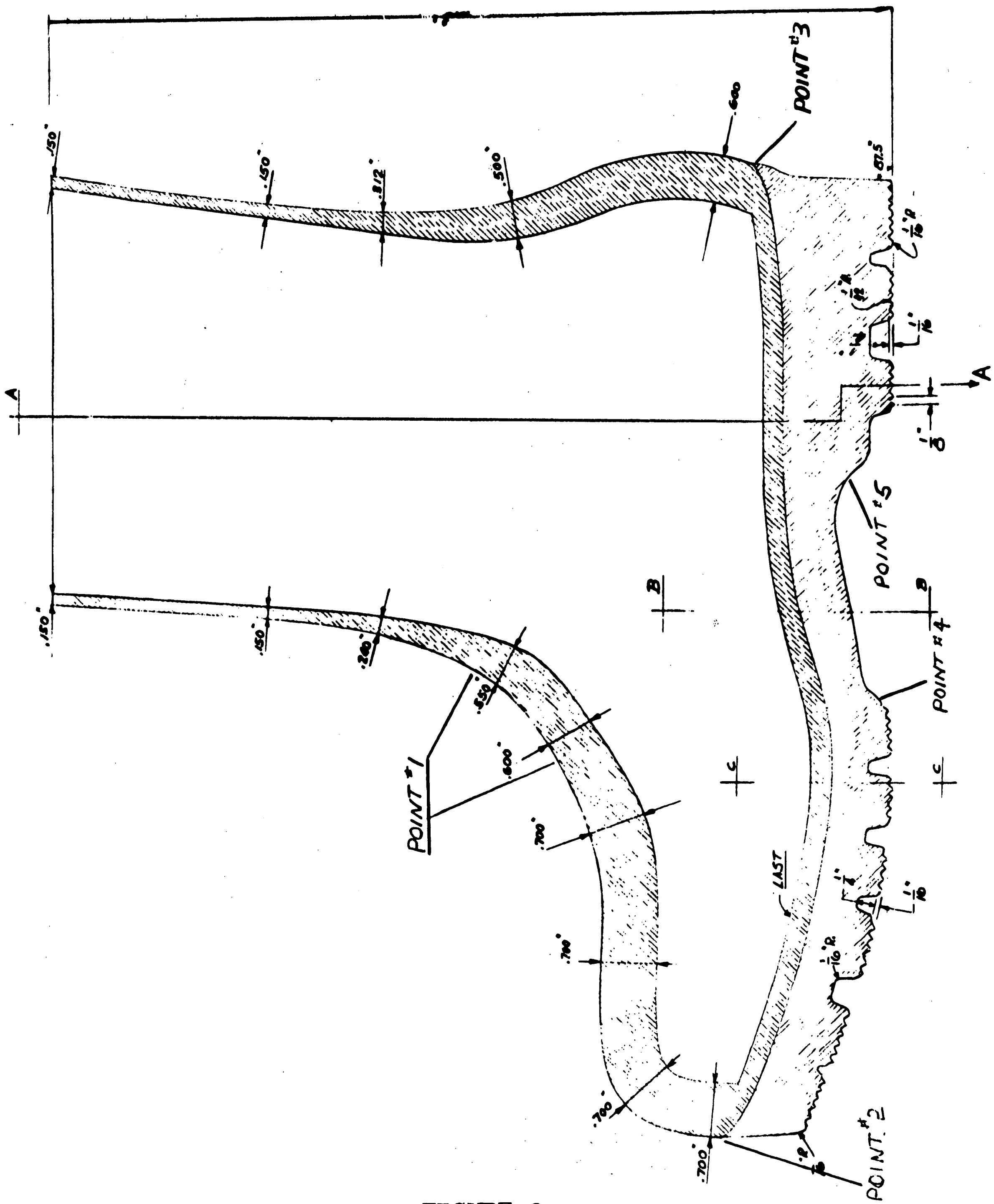

FIGURE 2
BOOT DESIGN WITH
PROPOSED CHANGES

DAAG17-71-C-0070). RT-4 has knurling to improve traction, a front groove one-eighth inch in depth and cleats in the ball area with one-eighth inch deep grooves. Design JA-1 is a modified RT-4 having a reduced number of mid-cleats and one-quarter-inch-deep grooves.

It was decided to standardize on Design JA-1. This outsole appeared to give the best combination of design features to accomplish the desired improvements in traction, flex crack resistance, and resistance to cleat chunking out.

II. MOLD AND MOLD CARRIER DESIGN

Mold design is very closely tied in with process design. For this reason the type of mixing equipment and method of mold filling are important considerations in mold and mold carrier design.

A. Molding Method - Contract DAAG17-72-C-0058

On the previous contract (DAAG17-72-C-0058) a Viking-Chase Pour Molding Machine was used to deliver the foam mixture. The Arctic boot wad molded in two steps with the higher density outsole being molded first in a mold set up as shown in Figure 8. After the outsole was cured far enough to allow removal of the outsole rings, the upper rings (Figure 9) were positioned around the last and were then bolted to the outsole plate. The upper foam compound which produces a lower density foam was then cast into the open fill port, and after the proper compound weight was delivered the port was plugged and locked and the foam expanded and filled the mold.

B. Evaluation of One-Quality vs Two-Quality Foam Injection

To simplify the material handling, metering and mixing, mold filling, and to work with a system that lends itself to automation it was decided to use the LIM (Liquid Injection Molding) equipment. This is a metering and mixing system that injects urethane foam compound into a mold under low injection pressure (20-25 lbs/in^2). It was decided initially to evaluate the LIM equipment using a one-quality foam injection where the outsole and upper are fabricated in the same injection. Later trials dealt with two-quality injections where the outsole or the upper was made on the first injection and the balance was made on the second injection. The following descriptions describe some of the more important variations tried and the results. The mold used was basically the same as the assembled mold shown in Figure 8. Instead of going through the step of making the outsole first and then the upper, the mold was completely assembled before any foam was injected and

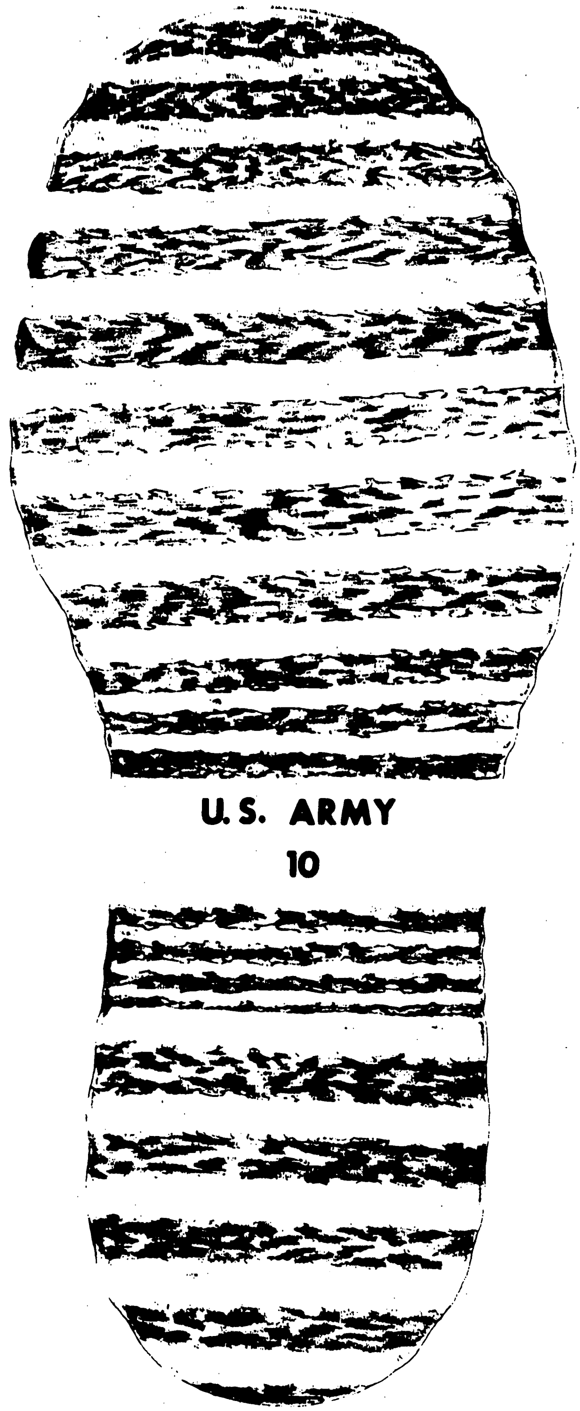

FIGURE 3
OUTSOLE DESIGN
#RT-1

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2-23-74

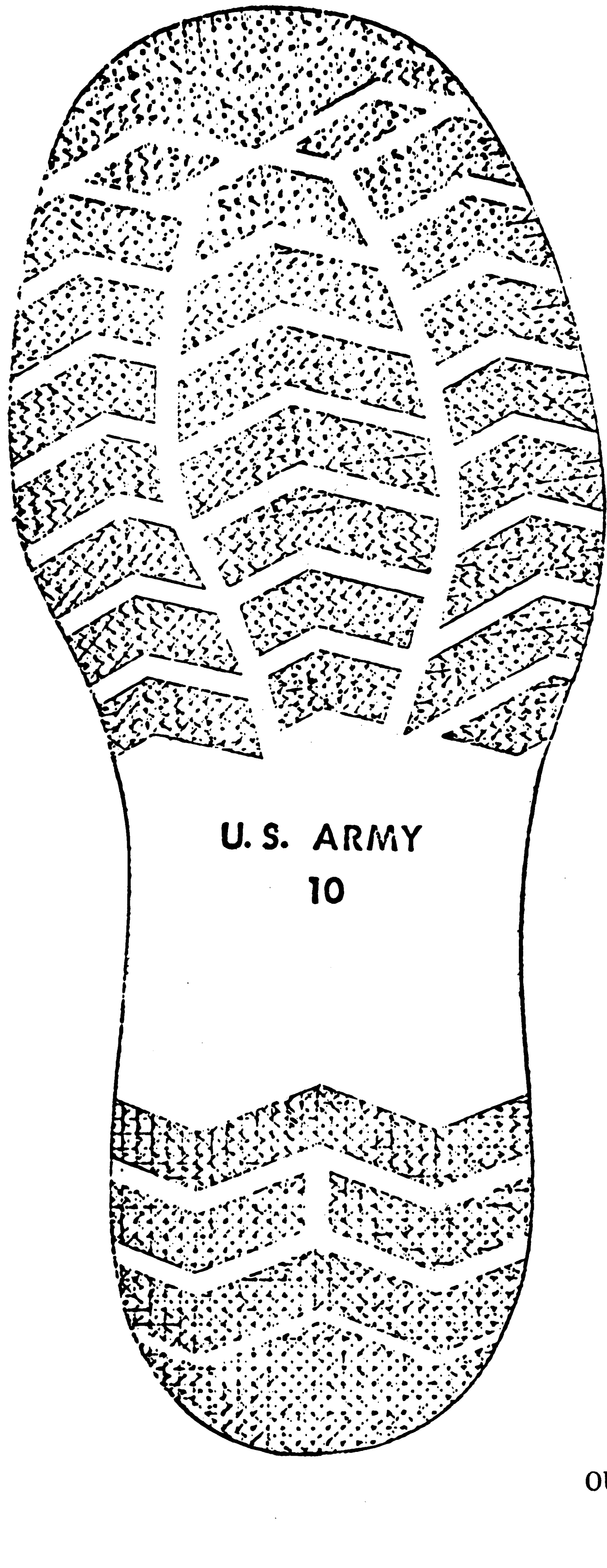


FIGURE 4
OUTSOLE DESIGN
#RT-2

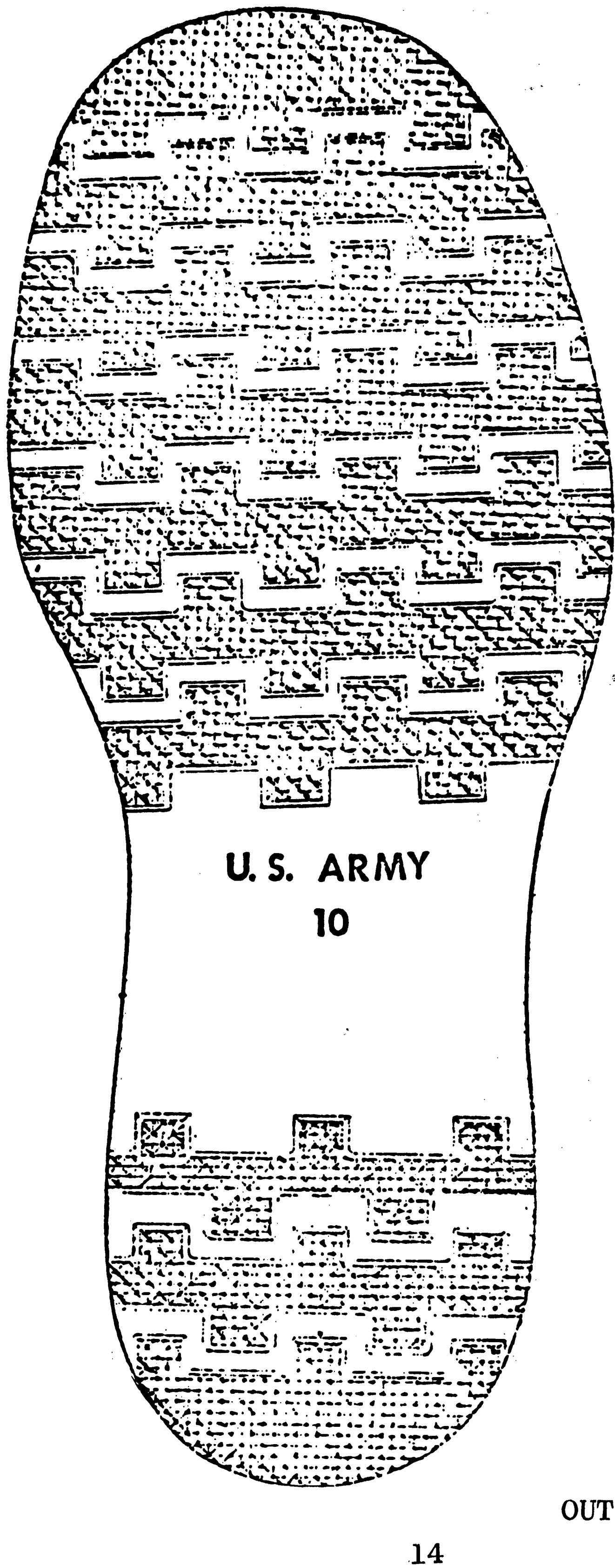


FIGURE 5
OUTSOLE DESIGN
#RT-3

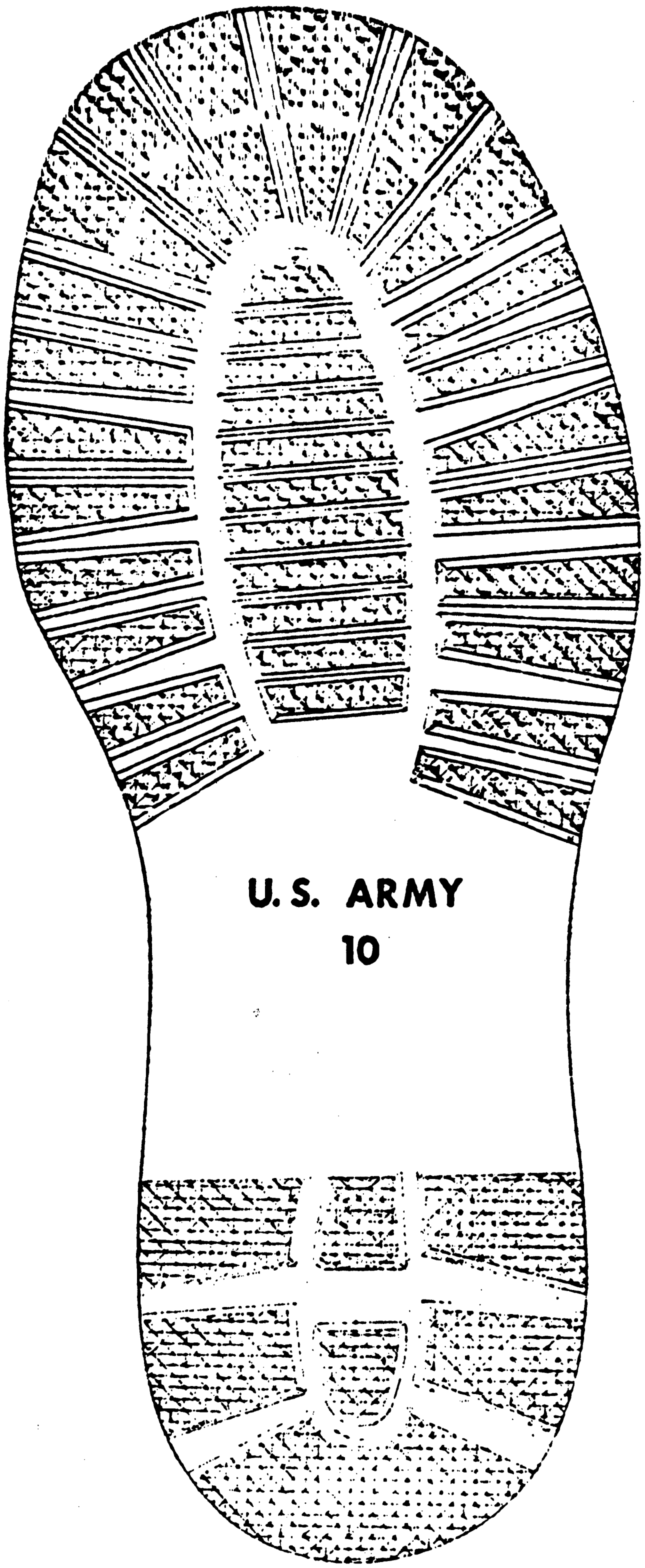
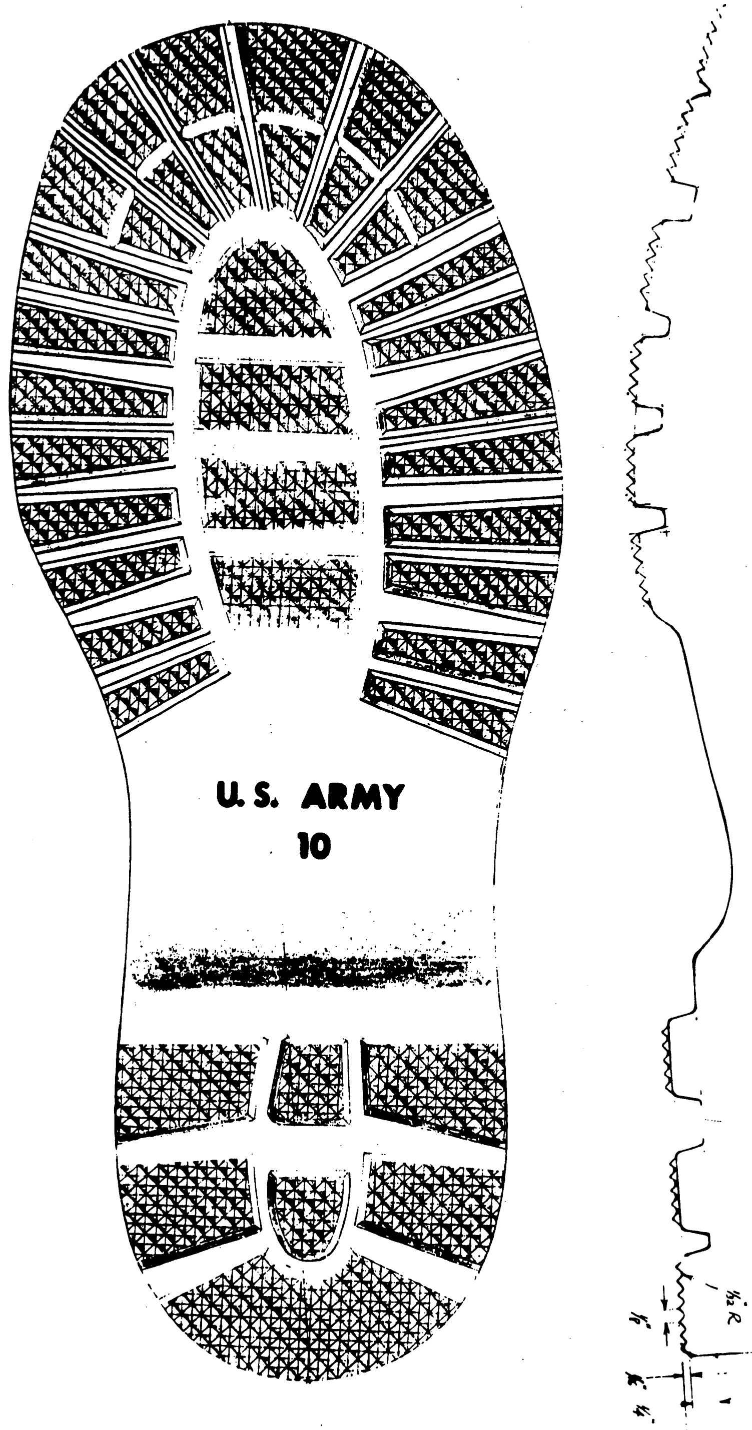


FIGURE 6
OUTSOLE DESIGN
#RT-4



REF. DWG. D-3222-301
2-23-74

FIGURE 7
OUTSOLE DESIGN
#JA-1

the complete boot was made in one shot.

1. A right size 10 boot mold was mounted on the turntable used in conjunction with the LIM equipment and a one-quality injection was made through the toe. Repeated attempts all resulted in boots only 60% complete. The foam did not flow enough to completely fill the upper section of the mold cavity.

2. The same mold used in (1) above was mounted upside down and a one-quality injection was made through the toe. The demolded boot had an incomplete outsole.

3. The injection port location was changed from the toe to the heel of the right boot mold. The port was a Y-type design with the initial portion of the port splitting off into two channels, one channel directed at the outsole portion of the mold and second channel directed toward the upper portion of the mold. A one-quality injection was made resulting in a complete boot; however the outsole was considered too low in modulus.

4. To increase the toughness of the outsole, a veneer outsole was laid into the mold before injection. The veneer outsole is a preformed, solid urethane, 60-70 gauge, outsole. The one-quality injection had to be shot through the toe port. The demolded boots had incomplete uppers.

5. A silicone rubber sheet was placed between the outsole plate and the upper halves to allow the outsole to be injected first. The first portion of the two-quality injection resulted in the outsole material forcing the silicone rubber sheet into the upper portion of the mold. A complete boot was fabricated having a distorted outsole/upper junction.

6. In this trial a silicone rubber gasket was placed between the upper halves and the outsole plate after an initial injection filled the mold with upper foam material. The gasket raised the foamed boot up and allowed the outsole material to flow around the outsole portion of the boot during the second injection. A complete boot resulted having a laminated outsole.

Results of these trials indicated that a two-quality injection was the most practical method for boot fabrication. To improve processing the upper would be made first with the injection being made in the heel area.

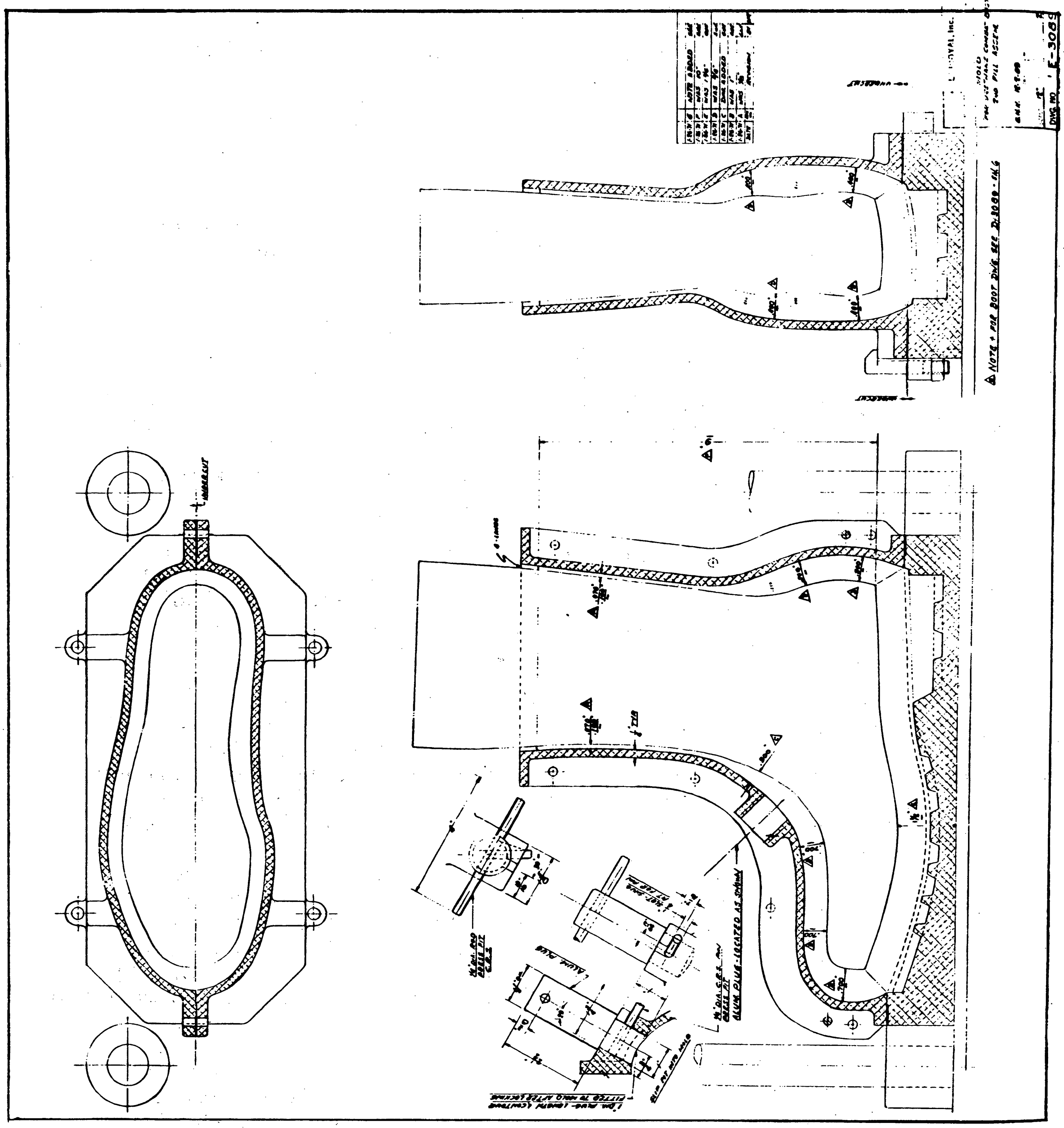


FIGURE 8
MOLD FOR FIRST FILL
ASSEMBLY E 3089-1

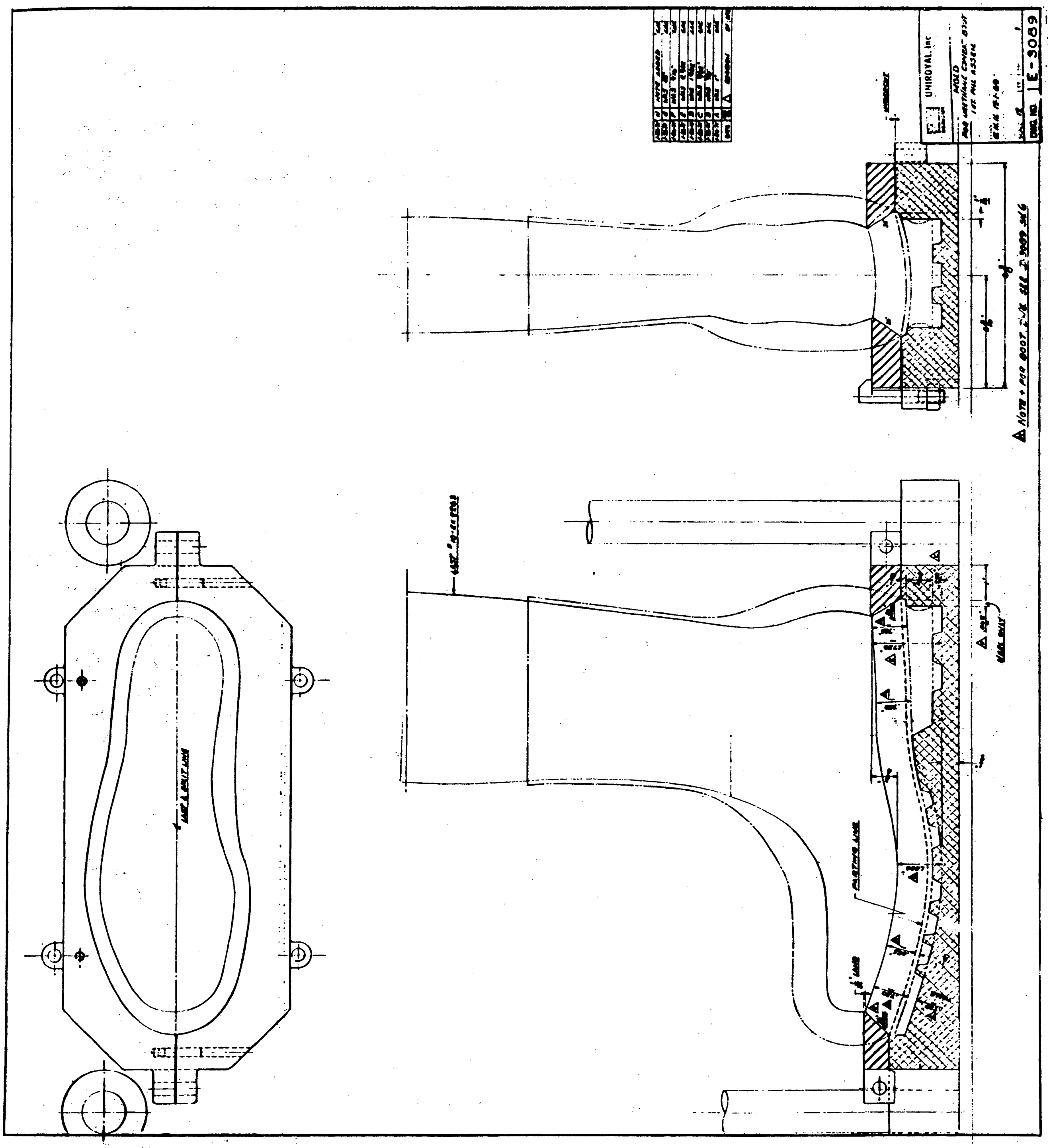


FIGURE 9
MOLD FOR SECOND FILL
ASSEMBLY E 3089-2

C. Mold Design and Molding Procedure for New Mold Design

After completing molding evaluation trials a pair of size 10 boot molds were designed incorporating the boot design changes discussed previously. They were to be constructed so that the two-quality foam injection method could be evaluated in conjunction with LIM equipment. The component parts of the mold are shown in Figure 10 and Figures 11, 11A and 11B. These molds were built by Desma-Werke, West Germany and utilized our basic design plus mold-making technology previously developed by Desma including the dual sole plate molding technique. The mold carrier was purchased from Desma and was designed and built by them.

The boot mold consists of solid machined parts except for the last which is cast. This compares to a completely cast mold as used in the previous contract (DAAG17-72-C-0058). The mold system consists of the last, upper rings and two sets of outsole rings and two outsole plates. One outsole plate is smooth and is used during the molding of the upper, the other has the embossed outsole design and is used during the molding of the outsole. All mold cavities are Teflon-coated to give easy release of the foam from the mold surface. The last has provisions for heating with cartridge heaters (Figure 10) and cooling by circulating water. The upper rings can be heated only. The outsole rings are mounted on plates in the mold carrier that can be heated but the outsole plate has no provision for heating other than conduction.

As shown in Figure 12 when the molds are set for the first quality injection which is for the upper, the upper rings are closed around the positioned last. The last positioning mechanism is made so that it will return to the same position each time assuring proper gauge. The sole plate and all other parts of the mold are locked in reference to the last.

The mold system also includes the dual sole plate set-up (Figure 12) including the mold parts and the mold station capability to shift the pairs of molds from side to side and up and down under the upper mold assembly. The dual sole plate operation involves one bottom sole plate duplicating basically the contour of the bottom of the last. This plate is held in position by a set of outsole rings which close against the bottom face of the upper rings. The first quality foam is injected with the last locked into position in the upper rings with the sole plate in the down position. The foam injection is made through the injection port in the

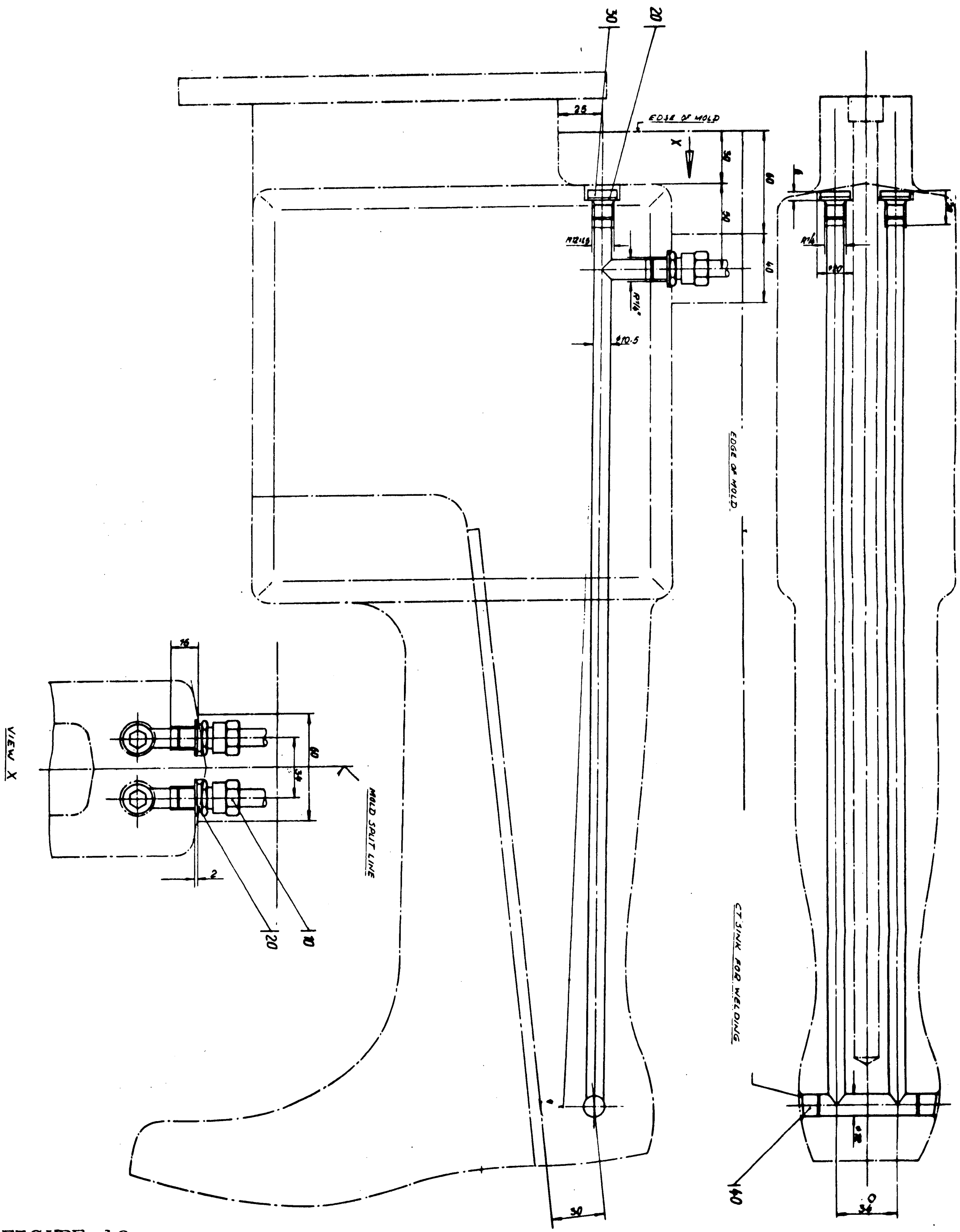


FIGURE 10
NEW LAST DESIGN

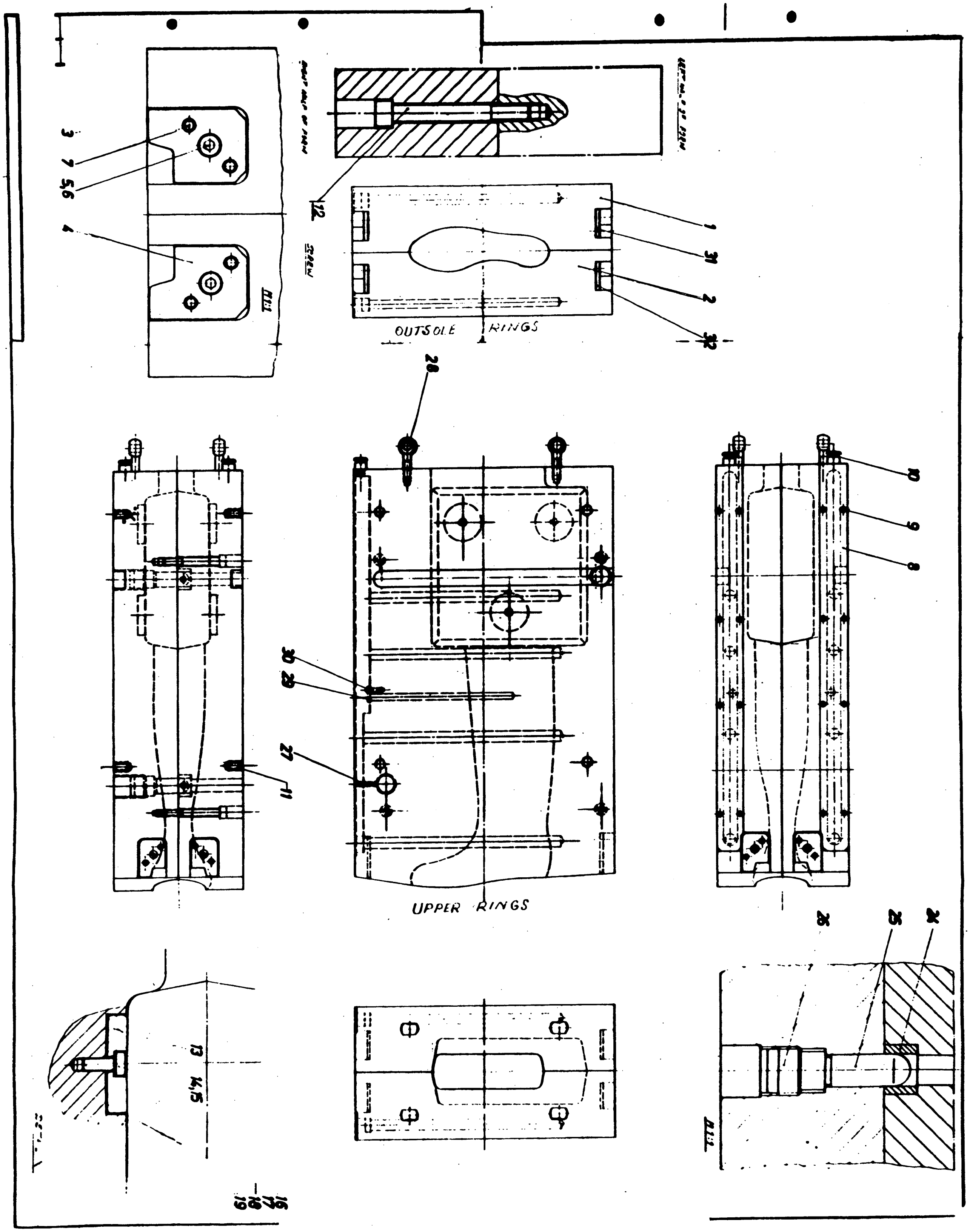


FIGURE 11
NEW UPPER MOLD & OUTSOLE
MOLD DESIGN

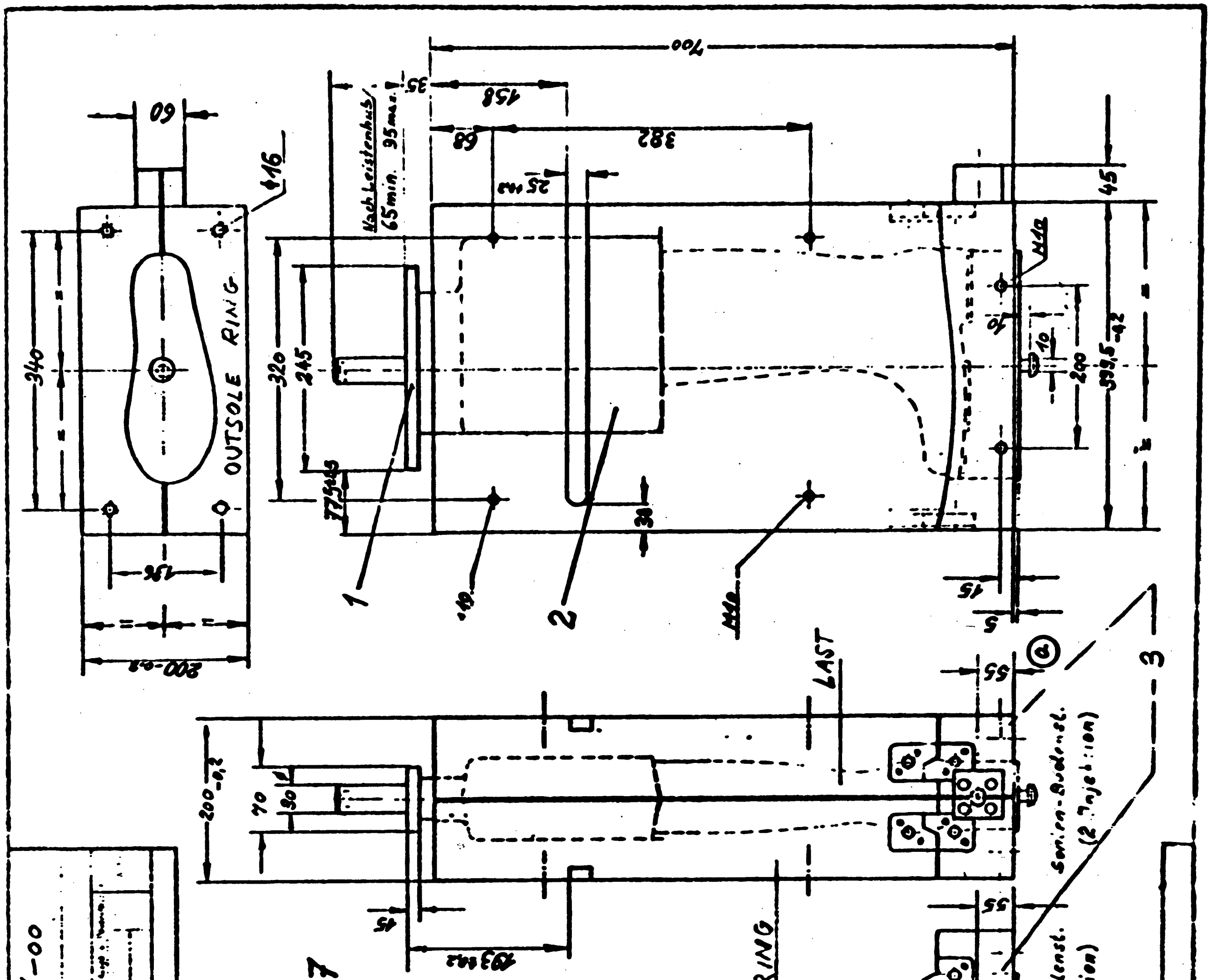


FIGURE 11-A
NEW UPPER MOLD & OUTSOLE
MOLD WITH OUTSOLE RINGS
IN POSITION

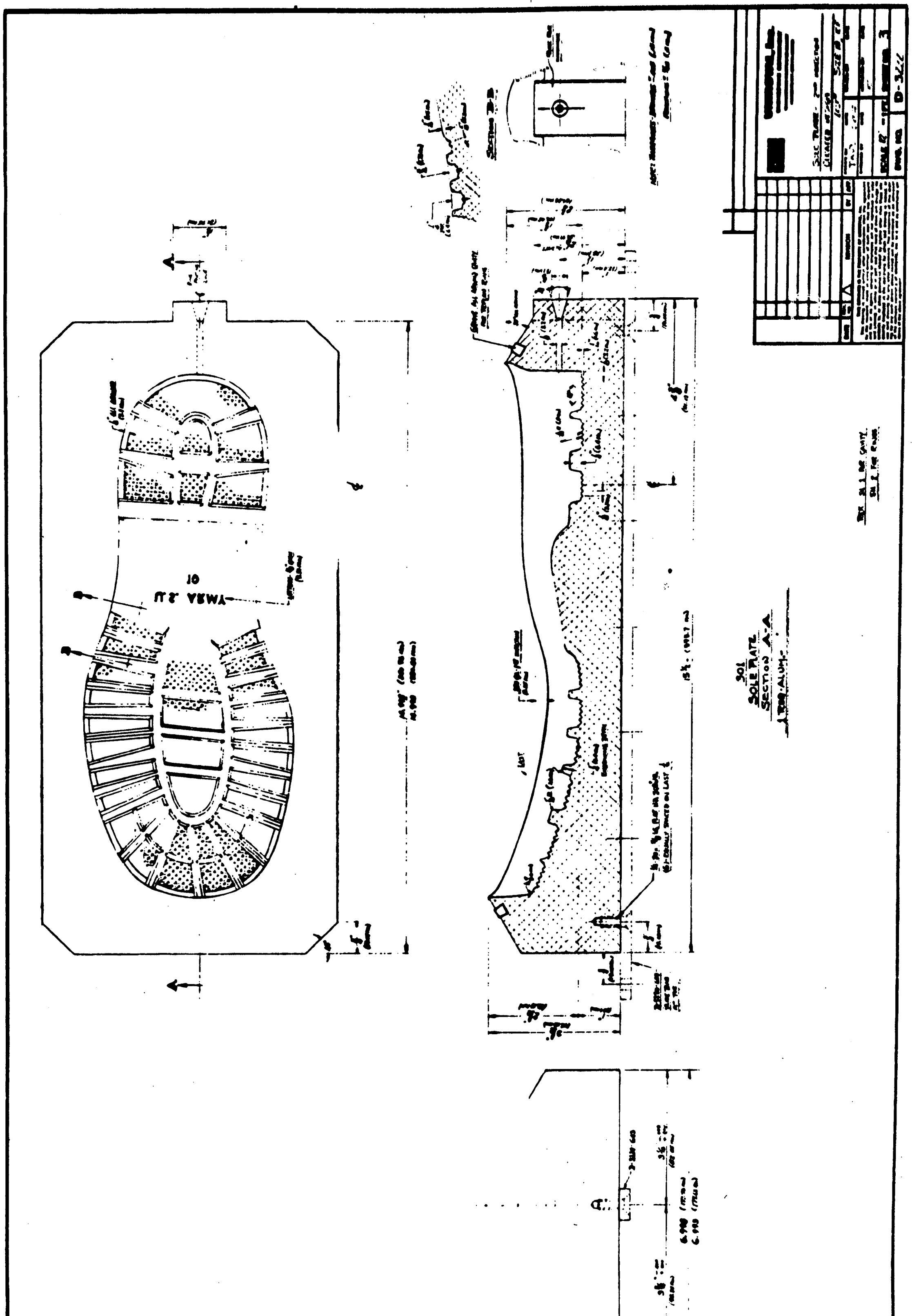


FIGURE 11-B
NEW OUTSOLE DESIGN

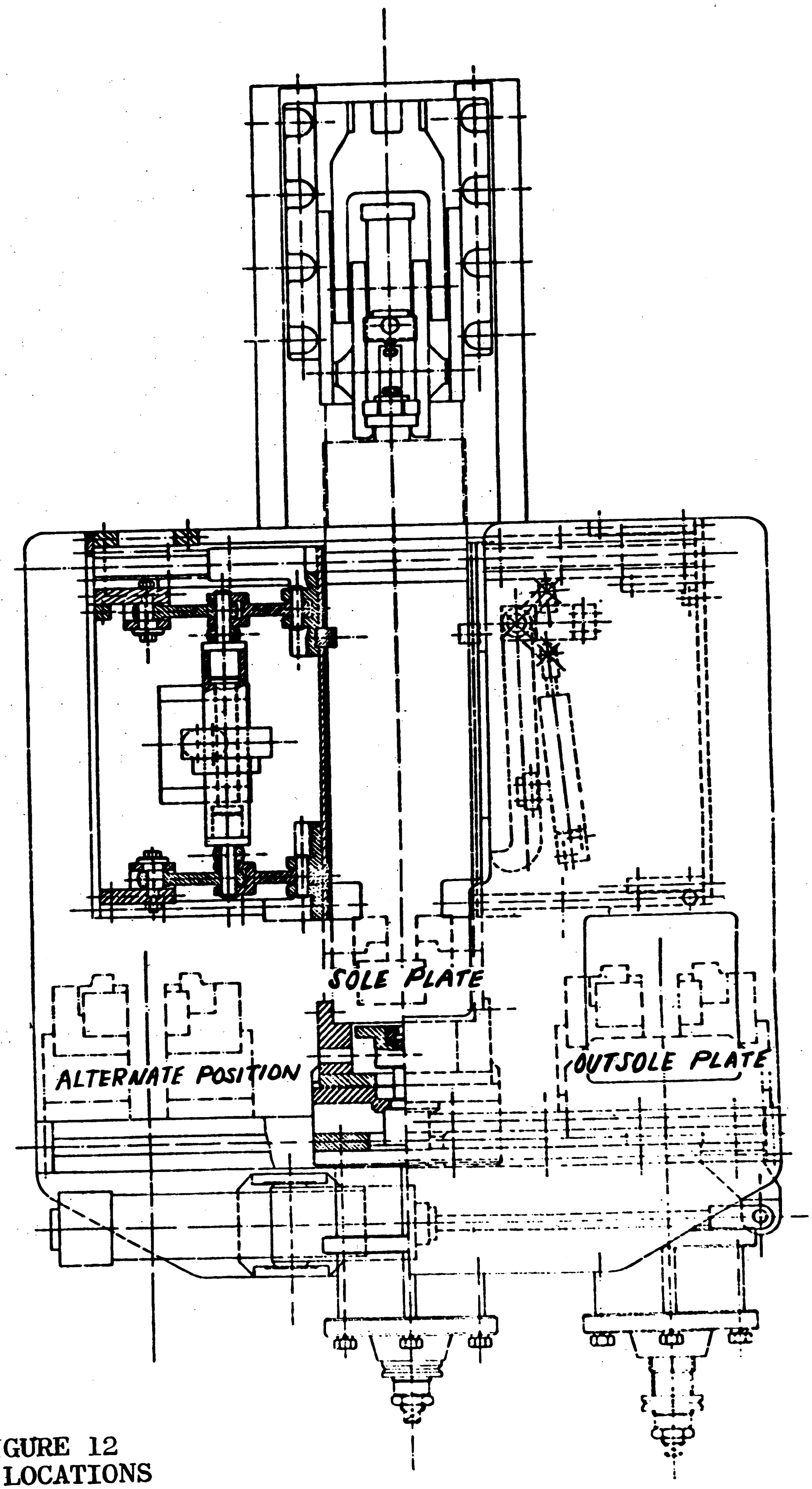


FIGURE 12
MOLD LOCATIONS
IN MOLD CARRIER

sole plate rings. As soon as the injection is complete, the sole plate is raised to seal off the injection port and form the correct cavity configuration for the upper.

After the first quality shot is complete and the foam is adequately cured, the first sole plate is dropped and the sole plate rings retract. The second set of outsole rings and the second outsole plate with the cleated outsole design slides into place as the first set slides to an open position. The outsole rings are closed against the upper rings. The outsole plate is in the down position. The second quality foam injection is made through the injection port in the outsole rings and the outsole plate raised to the proper position to give the correct outsole thickness and close off the injection port. After the foam is cured the outsole plate is dropped, the outsole rings are dropped, the upper rings are opened and the last with the boot on it retracts to a position outside the mold cavity for stripping, (Figure 13).

All parts of the mold are mounted in the mold station built by Desma that has the capability to move all parts in the proper direction and in the proper sequence of operation for molding a foam boot. A front and side view of the molds located in the mold station are shown in Figure 13. Air cylinders produce the required movement including the last introduction and withdrawal from the mold cavity, the opening and closing of the two pair of outsole rings as well as their shifting of position under the upper rings.

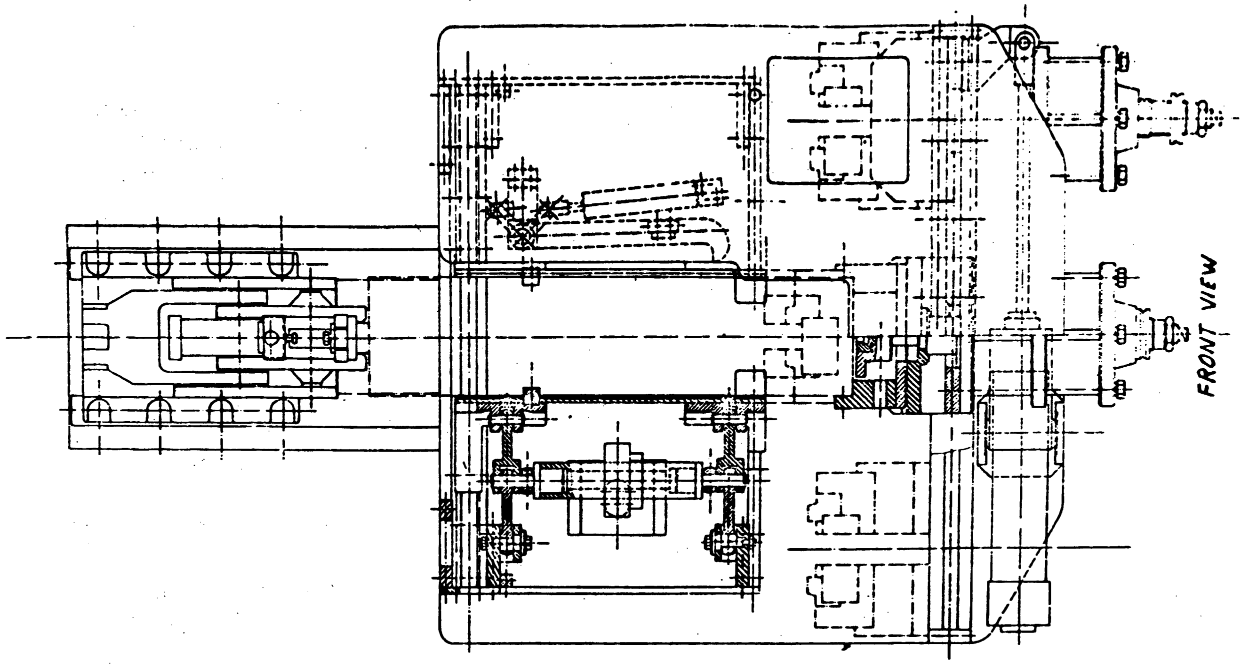
The molds and mold station provide the means for fabricating LIF boots with LIM equipment.

D. Mold Revisions

After preliminary molding trials were run mold changes were made to improve the operation.

1. Sealing surfaces around the injection port were machined to insure a good seal to eliminate any compound loss during injection.

2. Grooves approximately 3/8" wide by 1/4" deep were machined around the perimeter of the upper rings and the outsole plates so that Teflon gaskets could be incorporated and thus insure minimum flash at the mold joint lines. This change with the change in (1) above enabled us to accurately control boot component weight.



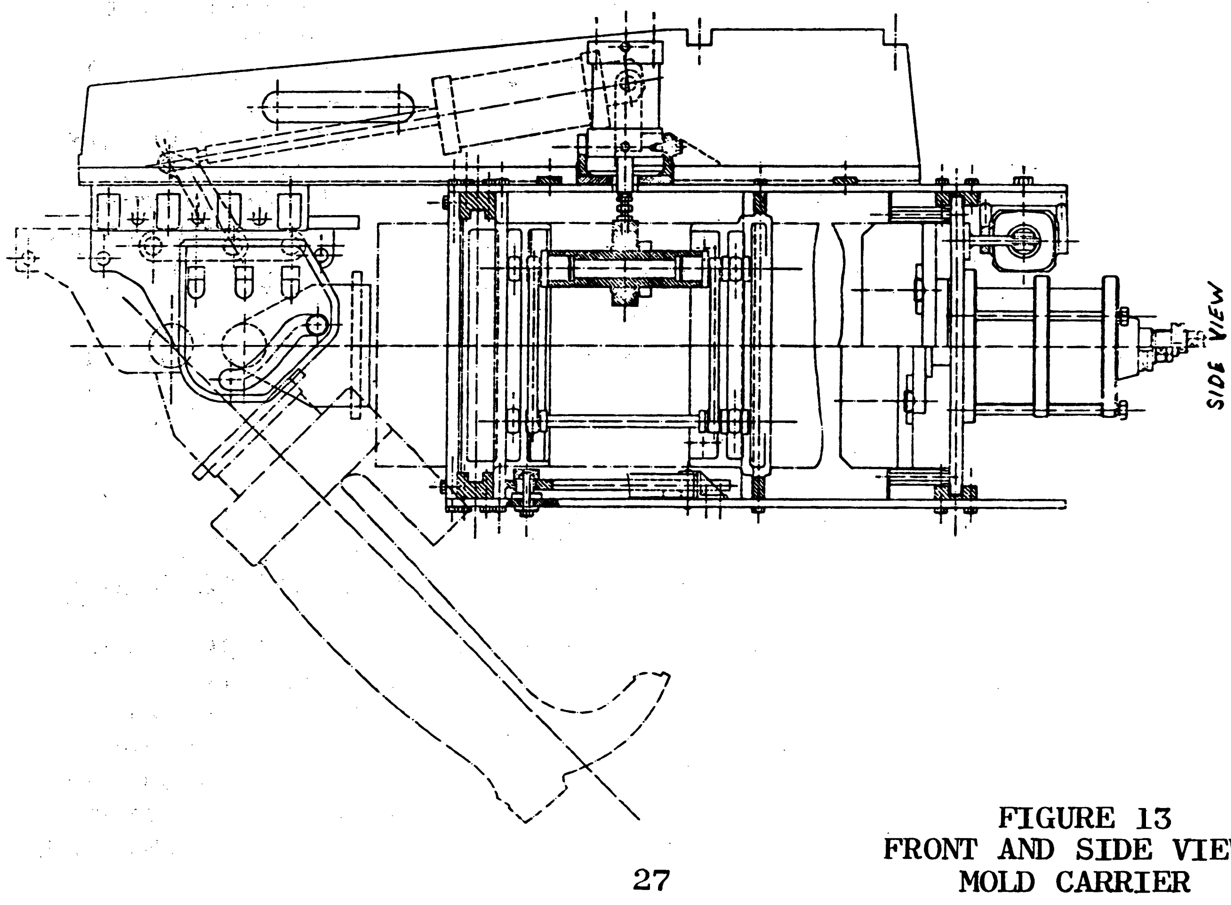


FIGURE 13
FRONT AND SIDE VIEW OF
MOLD CARRIER

3. Pins were installed in the upper section of the last to enable us to hold the socklining in place and to eliminate any change of socklining position that would cause wrinkles.

These changes gave improved quality boots.

III. LIQUID INJECTION MOLDING EQUIPMENT (LIM)

LIM equipment is used to mix and inject the required amount of urethane foam compound to properly fill the mold. This equipment shows the greatest potential for producing large numbers of parts at a reasonable cost. This is because of three primary factors. They are the reproducibility of production (which contributes to fewer rejects), the lower labor content per unit of production, and the ability of the equipment to handle fast reacting systems which result in shorter molding cycles.

The LIM foam mixing equipment used for compound mixing and molding evaluation, production of prototypes, and the production of 30 pair of test boots was made by Polyair Maschinenbau, Figure 14. The equipment is a foam mixing unit capable of supplying two or three components to a mixing head. The components are supplied from temperature controlled pots. Metering of the individual component streams is accomplished by the use of close tolerance gear pumps which give a high degree of accuracy. These pumps are tied together by a common drive chain that also goes around the main drive gear which regulates total output, Figure 15. Mixing is accomplished by passing the ingredients through a high shear mixer with the mixing screw turning at 18,000 RPM, Figure 16. The mixed compound is then injected into the closed mold in the mold station. The entire mixing unit carriage can be moved forward and back by an air piston so that the compound can be injected in the forward position and then retracted so that mold can be shifted and the mixing head can clean itself.

IV. ADAPTATION OF DEVELOPED CHEMISTRY TO LIM EQUIPMENT

A. Boot Foam Compounds Developed on Contract DAAG17-72-C-0058

The basic boot compounds developed in contract DAAG17-72-C-0058 were based on Vibrathane B-602. This material is a polyether urethane prepolymer which is a reaction product of polytetramethylene ether glycol (PTMG) and toluene diisocyanate (TDI). It is made with a free NCO of 3.3%. In addition to the base polymer in the compound were the curative, meta phenylene diamine (mPDA), a nitrogen gas producing blowing agent (Nitrosan)

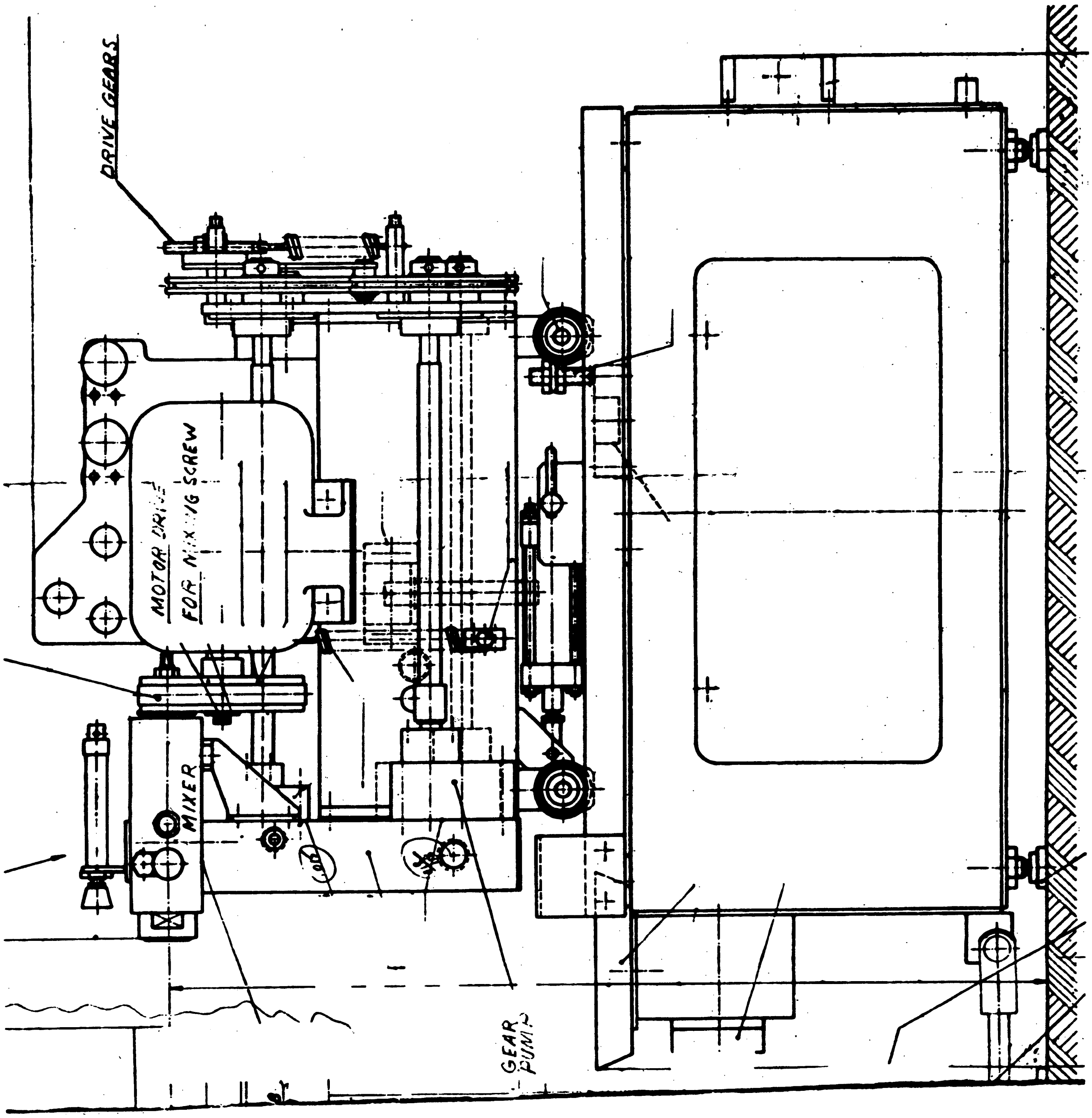


FIGURE 14
SIDE VIEW LIM INJECTOR

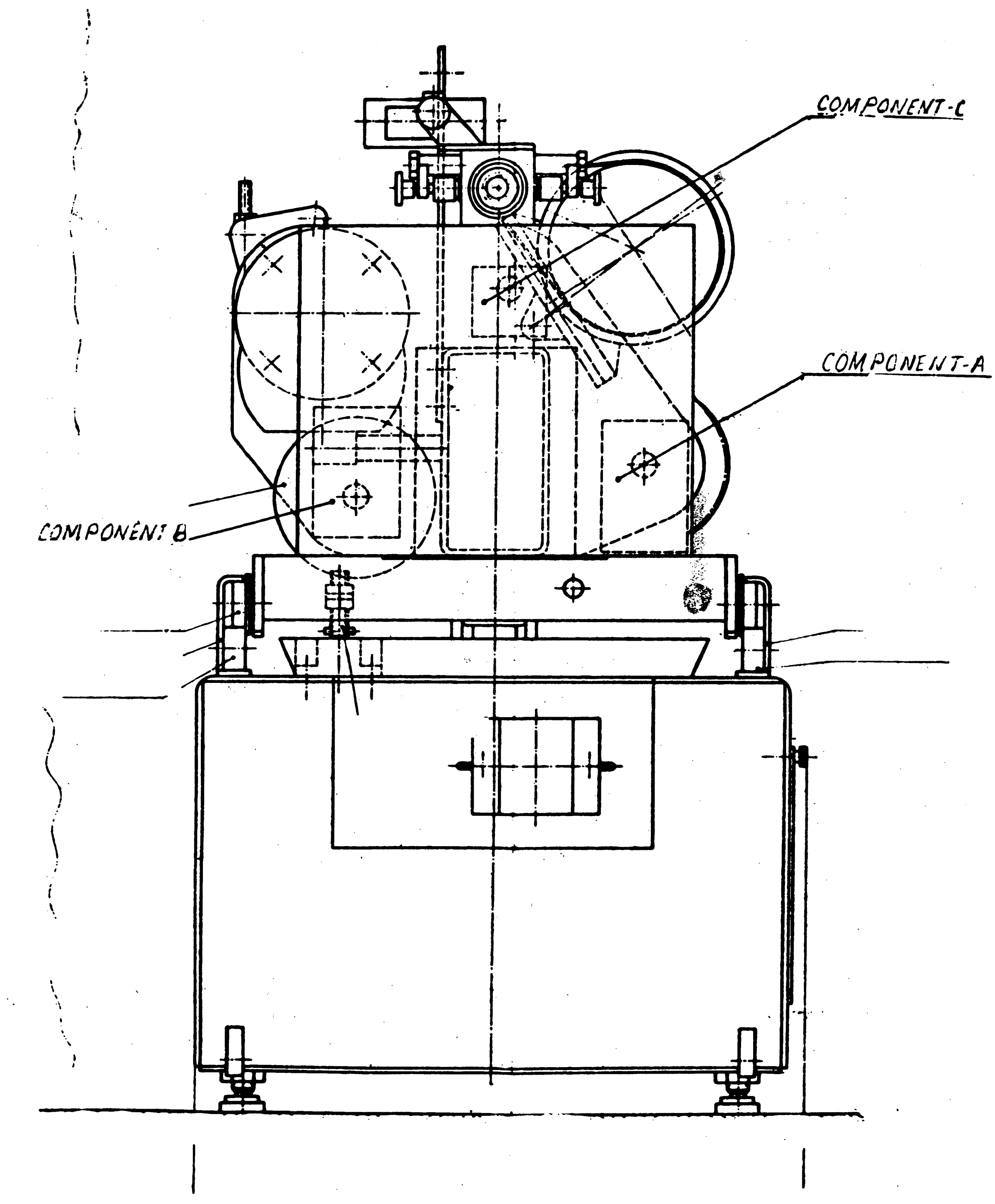


FIGURE 15
FRONT VIEW LIM INJECTOR

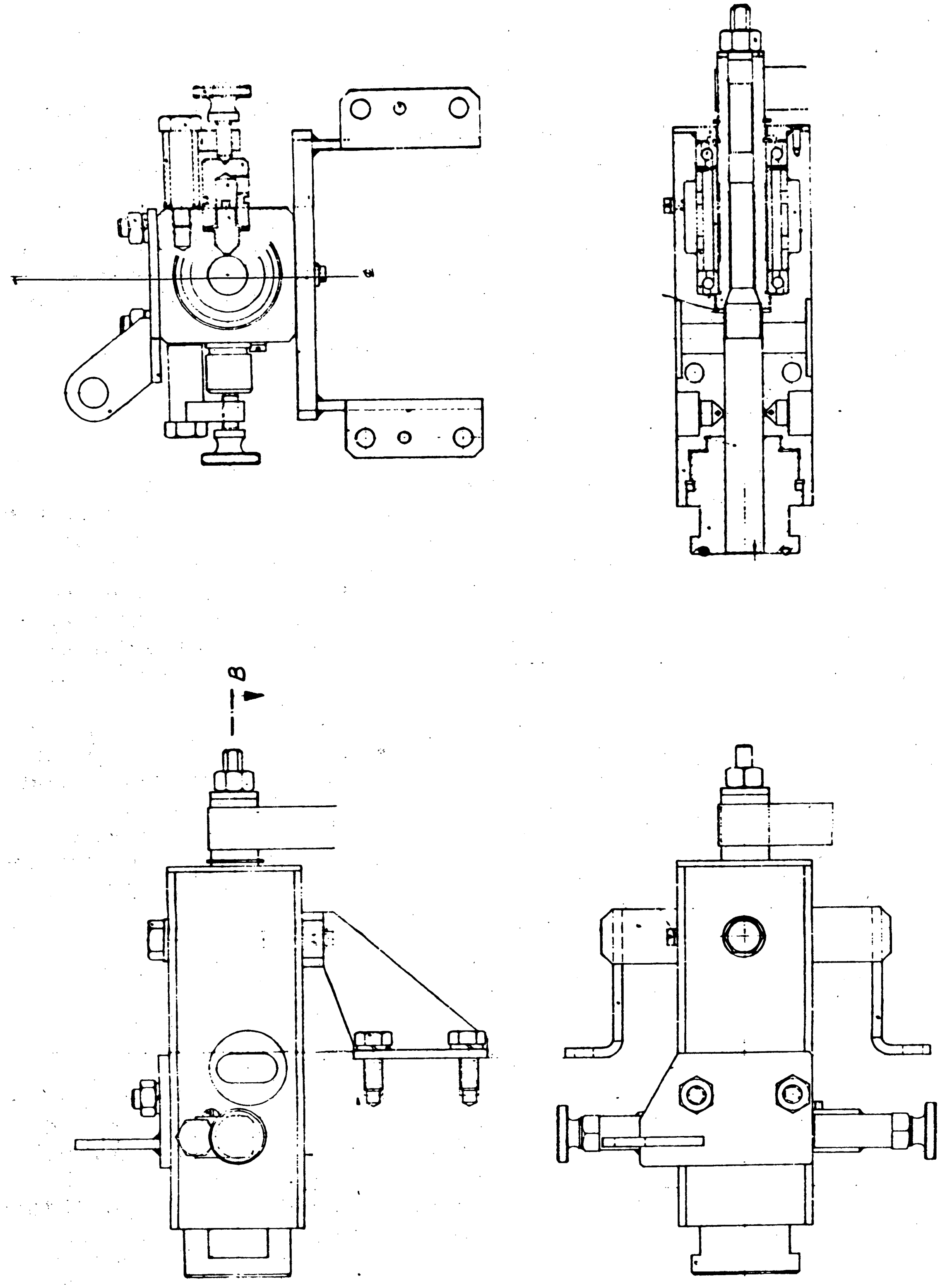


FIGURE 16
LIM MIXING HEAD

dispersed in a plasticizer (Santicizer 140), a silicone surfactant (SF-1079), and a black pigment dispersion (3041 Black). Both the upper and outsole were basically the same compound with the amount of blowing agent as the only significant difference.

PTMG was chosen as the base resin, since the beneficial effects of using this polymer in polyurethane elastomers requiring good low temperature flexibility have been established. Polymers made with this resin also have excellent resistance to hydrolysis as well as demonstrating good overall toughness.

B. Preliminary Compound Evaluation on LIM Equipment

The choice of PTMG was carried over to this contract because of its excellent properties. It was decided however that the high isocyanate levels necessary to use PTMG/TDI prepolymers on the LIM equipment would cause toxicity problems. Higher free NCO levels are necessitated because of the LIM equipment. The ideal mix ratio of the two major ingredients is 1:1. To obtain anywhere near this optimum ratio partial prepolymers must be used with free NCO's in the 10-20% range as compared to 3.3% in the previously used B-602. Because of the toxicity problems with TDI, use of prepolymers with MDI (diphenyl methane diisocyanate) was initiated. MDI has a considerably lower vapor pressure and its handling is less hazardous than TDI. The physical properties of PTMG-MDI polymers versus PTMG-TDI polymers are at least equivalent with no sacrifice in low temperature flexibility and with even an improvement in hydrolitic stability.

Some of the initial outsole and upper formulations evaluated on the LIM equipment are listed in Table 1. Formulation F-1 was an unsuccessful attempt to crosslink with mPDA (meta phenylene diamine). This was caused by the rapid reaction of the mPDA with MDI quasi prepolymer forming a cheesy compound. It was decided the best approach would be to use PTMG-MDI compounds chain extended with 1-4 butanediol. Formulations F-2 through F-7 involved varying the amounts of 1-4 butanediol and varying the density. F-3 exhibited the best physicals and was a good outsole candidate, however the density at 37 pcf (pounds per cubic foot) was higher than desired to keep total weight down. The amount of water could not be increased significantly to cause further expansion and reduce density because studies have shown the physicals of the foam would be lowered. Alternatives to lower the density involved blowing with a chemical blowing agent,

TABLE 1 - PRELIMINARY FOAM FORMULATION TRIALS ON LIM EQUIPMENT

	FORMULATIONS (PARTS PER HUNDRED POLYOL)								
	F-1	F-2	F-3	F-4	F-5	F-6	F-7	F-8	F-9
Reactive Ingredients									
PTMG .2000 (Polyol)	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
1,4 Butanediol (crosslinker)	9.02	9.85	7.96	6.92	11.56	7.68	8.20	5.17	8.20
mPDA (crosslinker)	4.64	----	----	----	----	----	----	----	----
SM (50% H_2O) (expanding agent)*	0.50	0.38	0.28	0.31	0.43	0.38	----	----	----
H_2O expanding agent)	----	----	----	----	----	----	0.41	0.80	0.41
MDI (isocyanate)	70.80	42.77	36.96	34.22	48.23	36.90	42.29	20.22	42.29
Additives									
Dabco (catalyst)	0.50	0.40	0.45	0.36	0.39	0.38	0.46	0.40	0.46
T-9 (catalyst)	0.13	0.11	0.04	0.09	0.11	0.10	0.11	0.06	0.11
DC-193(surfactant)	0.33	0.32	0.04	0.28	0.32	0.15	0.32	0.40	0.32
Pigment	----	----	----	----	----	0.97	1.03	----	1.03
Nitrosan (expanding agent)	----	----	----	----	----	----	----	----	varied
Physicals									
Tensile	----	----	875	700	----	1200	1325	400	----
Elongation	----	----	495	440	----	460	425	320	----
Tear (Die C)	----	----	181	150	----	200	199	58	----
NBS Abrasion	----	47.3	78.0	71.0	13.4	70.0	60.0	----	----
Flex (Polyair)	----	17,500	79,000	55,000	17,000	16,500	7,300	12,000	----
Density	----	37.6	37.0	38.0	30.0	41.0	36.0	15.0	----
Shore A Hardness	----	57	52	45	58	60	60	27	----
Comments	outsole- did not process	outsole type	outsole	outsole	outsole	outsole	outsole	upper type	upper- did not process

*Emulsifying Agent - 50% Water

Nitrosan, instead of water. F-8 was the upper formulation used in the processing studies mentioned earlier to determine if a one-quality or two-quality injection system was preferable.

Formulation F-9 was evaluated on the Polyair injector that has three-component capability. This was necessary since the Nitrosan is heat sensitive. Trials were made in an effort to run a Nitrosan-S-140 plasticizer mixture through a cooled third stream supply to the mixing head. This evaluation was unsuccessful since the Nitrosan stream backed up into the prepolymer stream causing inconsistent metering. A check valve was requested and installed.

At this point it was decided to concentrate on upper quality foam. Formulations F-10 and F-11 in Table 2 were evaluated on the LIM capable of delivering three individual compounds to LIM mixing head. F-10 was also used to evaluate the third stream capability of the injector as well as Nitrosan as a blowing agent introduced in the third stream. The revamped fittings of the third stream allowed proper metering; however, the amount of blowing agent dispensed was too small even at maximum output which necessitated replacing the original 0.6 cm^3/rev. pump with a larger output pump (3.0 cm^3/rev.). Low density foam was made at medium output of the blowing agent. The third stream was now considered suitable for cooling and accurately dispensing the proper amount of blowing agent for low density upper foam.

C. Compound Evaluation of Solvent Type Blowing Agents

It was decided that compound developments should include investigation of additional inert blowing agents because of some of the processing problems being encountered with Nitrosan. When using Nitrosan with the PTMG/MDI/1-4 butanediol system (F-11), the Nitrosan was blowing at a slower rate than the compound was curing causing ruptured cells and striations in the foam. This occurred even at longer cure times and varying process temperatures. Previous work had also shown that residual Nitrosan sometimes causes problems in the finished boot dimensions and its blowing efficacy had been difficult to control. Inert blowing agents such as Freon (trichloromonofluoromethane) could provide the following:

1. minimal loss of blowing efficacy

2. no effect of blowing agent on the finished boot

3. low processing temperatures

TABLE 2 - UPPER FOAM FORMULATIONS

	Formulations (Parts Per Hundred Polyol)								
	F-10	F-11	F-12	F-13	F-14	F-15	F-16	F-17	F-18
Reactive Ingredients									
PTMG 2000 (polyol)	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
1,4 butanediol (chain extender)	6.75	6.75	18.75	25.00	25.00	25.00	25.00	15.00	15.00
CP4701 (crosslinker)	---	---	25.00	---	---	---	---	---	---
TMP (crosslinker)	2.50	2.50	---	---	---	---	---	---	---
PTMG/MDI 19.75% NCO (prepolymer)	65.03	65.03	113.35	---	---	---	---	---	---
PTMG/MDI 19.93% NCO (prepolymer)	---	---	---	137.57	137.57	137.57	137.57	90.73	90.73
Additives									
Dabco 33LV (catalyst)	---	---	0.63	---	---	---	---	---	---
Dabco (catalyst)	---	---	---	0.58	0.58	0.58	0.58	0.50	0.50
T-9 (catalyst)	0.12	0.12	0.10	0.17	0.17	0.17	0.17	0.13	0.13
DC-193 (surfactant	0.40	0.40	---	---	---	0.83	0.17	0.10	0.10
Methylene chloride (blowing agent)	---	---	12.50	---	---	---	---	---	---
Freon 11B (blowing agent)	---	---	6.25	33.30	---	---	---	---	16.70
Freon 113 (blowing agent)	---	---	---	---	33.30	33.30	33.30	33.30	16.70
Nitrosan (blowing agent)	3.00	7.00	---	---	---	---	---	---	---

4. integral skin while maintaining 10-12 pcf average density. This skin will give additional puncture resistance.

Past experience had shown that non-shrinking foam with a tough integral skin could be made with a methylene chloride/Freon combination. Formulation F-12 was an attempt to make integral-skinned foam from that blowing agent combination. F-12 was difficult to process and resulted in foam with poor cell structure. Feeling that perhaps the ruptured cells in the F-12 foam were caused by the methylene chloride, F-13 was made with only Freon 11B in the hardener. The F-13 formulation mixed with a lab air stirrer resulted in good quality foam. The same formulation processed on the LIM injector exhibited foam collapse. In F-14 the Freon 11B (Boiling Point 75°F) was replaced by Freon 113 (Boiling Point 117°F), but the foam still collapsed when processed on the LIM injector. Formulation F-15 was F-14 with silicone surfactant added to the hardener. The resultant foam did not collapse but exhibited foam shrinkage on curing. F-16 had a reduced amount of surfactant and processed well on the LIM resulting in good quality, integral-skinned foam.

The F-16 foam was free-blown in paper cups. Attempts to make a test slab in the aluminum slab mold sprayed with silicone release agent failed - the foam collapsed. Subsequent trials were made with (1) a silicone rubber mold and (2) a urethane mold sprayed with silicone release agent. Excellent integral-skinned foam was made in each mold. F-16 compound was injected into the aluminum slab mold covered with a dry release agent (fluorocarbon). A good foam slab was made.

Although a free-blown sample of F-16 foam had adequate flexibility, the integral-skin slab was too rigid with poor flex properties. To make the foam more flexible the amount of 1,4 butanediol was reduced in formulation F-17. The free-blown F-17 sample and test slab were both flexible enough and exhibited good flex properties. The free-blown sample had a 5 pcf average density while the test slab had a 11 pcf average density.

Trials were now undertaken to evaluate the upper foam formulations previously mentioned as to foam rise, cure time, mold fill, mold temperatures and skin thickness in the Arctic boot configuration. A modified right, size 10, mold was used during the trials.

Trial 1 - Formulation F-16 was injected into the boot mold with the mold temperature at 100°F. The mold filled properly. The foam had a tough skin but collapsed upon curing. The foam collapse was possibly due to residual silicone mold release and/or improper mold temperature.

Trial 2 - The above trial was repeated with the mold temperature at room temperature. The degree of foam collapse increased.

Trial 3 - Trial #1 was repeated with the mold temperature at 140°F. There was minimal foam collapse and well-formed integral skin.

Trial 4 - Formulation F-18 (Table II) was injected into the mold at 160°F. There was no foam collapse and minimal integral skin.

Some conclusions were made after performing the above trials. With the proper mold temperature and Freon type, a flexible upper foam can be fabricated having an integral skin. The higher the mold temperature the less skin thickness is formed. Additional trials indicated a temperature of 115-140°F would give a skin the thickness of .040"-.060". The core density is 8-10 pcf giving an average density of 12-14 pcf.

At this time the new design boot mold for LIM-LIF and the mold station were received from Desma-Werke, West Germany. It was installed, and molding trials were initiated. Because of the encouraging results in molding with Freon blown PTMG-MDI-1-4BD for upper foam systems, it was decided to make the prototype boots with this basic system. The outsole would be made with a water blown system.

This results in a uniform density gradient, and the urea linkages formed during the reaction of water with MDI give added toughness to the resulting foam. The first boot was fabricated on the new equipment in mid-July 1974. It was a two-quality injection using Freon 113 for expanding the upper and water for expanding the outsole.

A great deal of time and effort was expended attempting to mold consistently good quality boots with the Freon blown upper compound. Partial success was attained in that reasonably good physical properties were attained, but the quality of the boots produced was variable, and regardless of formulation modifications, varying of process conditions including ingredient temperatures, mold temperatures, injection rate,

injection position, etc., acceptable quality boots could not consistently be made.

The physical properties of these Freon blown LIM-LIF boots were as follows:

UPPER FOAM (F-17)

Tensile strength	(skin layer)	4000 psi
Elongation	(skin layer)	500%
Tear strength	(skin layer)	450 lb/in.
Tear strength	(inner foam)	12 lb/in.
Average density		12 pcf
Compression Deflection at 25%		2.8 psi
Compression Set at 50%		13.6%
Deflection at RT		4.0 psi
at $-20^{o}F$		15.0 psi

OUTSOLE FOAM (F-3)

Tensile strength	970 psi
Elongation	440%
Tear strength	160 lb/in.
Density	35 pcf
Shore A	55

Subjective evaluation using "feel" by hand indicated the boots were stiffening at -20^{o} F. In addition the water pickup was higher than the allowable goal in the specification.

In addition to prototype boots a number of boots with the Freon blown uppers and water blown outsoles were produced towards the 50 pair for test. A majority of the boots had some defects and where voids were formed during the molding they were repaired by filling with a urethane latex and then

buffing to the proper contour. As the boots were being molded, changes in formulation and processing continued to be made in an effort to improve quality and physical properties. Development work and processing of boots toward the 50 pair for test were being done simultaneously. This turned into a completely unworkable setup and satisfactory progress was not being made towards completion of the contract.

D. Extension of Contract Deadline

On November 13, 1974 a meeting was held with the Project Officer on this contract. At this time it was decided because of several unresolved problems in processing and because the quality of the boots being made was questionable, the Alaskan Test should be postponed.

The major problem areas discussed that required answers were as follows:

1. Boots were not flexible enough at -20^{o}F after a 2-hour exposure.
2. Some delamination between the socklining and upper foam.
3. Void formation in the boot uppers that required repairs.
4. Occasional loose skin on the outsole.
5. Water absorption higher than allowable.

After our discussions, a request for an extension to the contract was made so that Uniroyal could return to laboratory evaluation without being under the immediate pressure of producing boots for service testing. Additional costs above the contract were to be absorbed by Uniroyal. This request was granted.

E. Review of Base Compounding Ingredients

After postponement of the test, compounding and processing studies were made to correct the deficiencies in the boot. One of the major problems was that the boot was too stiff when exposed to a temperature of -20^{o}F for 2-hours. Properties of our base materials were reviewed and it was felt that these materials were the best choice to perform satisfactorily the service requirements of this application. The base polyol resin, PTMG (poly tetramethylene ether glycol) and the isocyanate,

MDI (diphenyl methane diisocyanate) were retained. It was felt that some improvement in low temperature flexibility might be accomplished by modifying the chain extender. A study was made of chain extenders and it included 1-4 butanediol, 1-6 hexanediol and 1-9 nonanediol. These extenders were used at varying levels and in combination with each other. Films with no blowing agent were made with these compounds so that low temperature flexibility tests could be run utilizing the Gehman Test which indicates change in stiffness as temperature is varied.

In addition to the chain extender modifications, trials were also run with a portion of the PTMG (12%) replaced with a hydroxy terminated polybutadiene resin. The net result of the screening tests indicated the best overall performance of a PTMG-MDI based compound including both processing characteristics and low temperature flexibility was with 1-4 butanediol as the chain extender. The level indicated was 0.2 of an equivalent weight of butanediol based on a formula with 0.1 of an equivalent weight of PTMG.

Trials were resumed making foams with the best chain extender PTMG/MDI combination. It was decided to work on the upper foam composition first. All recent boot upper making had been done using Freon (chlorotrifluoromethane) as the blowing agent so initial foam work was resumed with this blowing agent. Previous results were confirmed. Consistently good quality foams could not be made using Freon. Foams were not flexible enough at -20°F and socklining adhesion was still a problem. In addition to the difficulty of producing good quality foam, test results indicated that water absorption values could not be made acceptable for the Arctic boot application. Since this is a life-limb application it was decided a switch must be made to a different blowing agent that produces a foam with a high percentage of closed cells. The only way this could be accomplished was using a chemical blowing agent such as Nitrosan.

F. Upper Foam Compound Development Using Nitrosan as Blowing Agent

Upper foam development work was switched to PTMG/MDI compounds with Nitrosan as the blowing agent. It was found major modifications in compounding were necessary since the compound must reach a temperature of 190°F to initiate the decomposition of the blowing agent. The temperature must then reach above 200°F to complete the decomposition. In order to give the compound additional strength at these temperatures and to stabilize the foam structure it was necessary to add a small

amount of TMP (trimethylolpropane). This is a trifunctional chain extender and is used to regulate the molecular weight per crosslink. With the addition of TMP the amount of 1-4 butanediol was reduced to keep the level of chain extender constant.

Basic compound temperatures (other than the blowing agent) had to be raised to the 190-220°F range and mold temperatures had to be raised to the 170-234°F range. The hardener (which contains polyol, chain extender, catalyst and any other required additives) and prepolymer components were heated in the supply pots of the Polyair LIM foam mixing machine and the Nitrosan (in plasticizer S-140) was added as a third component and was kept at 60-70°F by a cooling water jacket. The hot and cold components were joined at the mixing head and immediately injected into the hot mold. Preliminary upper foam compounds were made and a fine closed-cell foam resulted. Initial foams had a softer feel at -20°F and water absorption tests indicated a low water pickup that was within the required specification.

It was found three primary variables affect foam properties:

1. Amount of short molecular segments (chain extender).

2. Molecular weight per crosslink (M/C).

3. Compound and cure temperature.

The variables in 1 and 2 above were studied by varying the ratios of PTMG-chain extender-MDI in foam compounds. To identify these mole ratios, numbers indicating the ratio of each ingredient are written in a sequence duplicating the above order of listing. Therefore, a 1-2-3 compound is composed of 1 mole of PTMG, 2 moles of chain extender, and 3 moles of MDI. The ratios were varied from 1-1-2 to a high of 1-3-4. The foams produced had noticeably different properties and required quite different process conditions and formula variations in catalyst to make acceptable structure foams. The 1-1-2 gives a low modulus foam that has an excellent soft feel but lacks toughness. On the other hand the 1-3-4 ratio foam has a high modulus and is a very tough foam. The 1-1-2 foams feel flexible at -20°F after 4 hours but the 1-3-4 foams tend to stiffen at -20°F.

Foams with intermediate properties can be made using intermediate mole ratios. Boot uppers made of .1-2.3-3.3 were still too high modulus, and foams of 1-1.6-2.6 were felt to be a little too soft. The best combination of properties

combining overall toughness and flexible "feel" at low temperature that processed satisfactorily when molded in the boot configuration was 1-1.8-2.8 and this was selected as the mole ratio for the upper foam.

Various type catalysts were evaluated in these upper foams in order to get the proper balance of gel rate and cure rate to correspond with the decomposition of the blowing agent and flow within the mold. Amine catalysts when used by themselves gave a slow cure but a fast initial gel which inhibited flow in the mold. For this reason tin catalysts by themselves rather than in combination with an amine were tried. Tin catalysts included T-12 (dibutyl tin dilaurate), T-9 (stannous octoate) and UL-1, UL-2 and UL-22 (modified tins). T-12 gave the best results in that it is stable at the high compound feed temperatures and at the correct concentration produces a foam with the proper rise and cure time so that an acceptable foam results. The T-12 performs particularily well when foam temperatures reach the 180°F range which is the mold temperature being utilized.

It was also found during processing evaluation of the varying mole ratio compounds that higher compound temperatures and mold temperatures gave better low temperature flexibility of the resulting boot at -20°F. Identical compounds run at lower compound supply temperatures were not as flexible at -20°F after 4 hours conditioning. These compounds appear to remain more homogeneous at higher temperatures.

As the amount of short molecular segments increases, higher cure temperatures and catalyst levels had to be used to obtain a homogeneous elastomer throughout the cure cycle. For the soft 1-1-2 compound the critical temperature appears to be about 120°F. For the much harder tougher 1-3-4 compound supply temperatures up to 250°F are necessary.

After selecting the 1-1.8-2.8 mole ratio for use in the boot upper, the compound and processing conditions were finalized, so that excellent quality uppers could be produced repetitively. Adhesion of the foam to the socklining is excellent.

G. Finalized Upper Foam Formulation, Processing Data and Physicals

The formula selected for the upper formulation is as follows:

	Equivalents	Parts
PTMG (2000 MW)	0.100	100.0
1-4 Butanediol	0.1511	6.8
TMP	0.0266	1.2
MDI	0.2824	35.3
DC-193 (Silicone Surfactant)		0.64
T-12 (Catalyst)		0.02
Nitrosan (Blowing Agent)		3.9
Santicizer 140 (Plasticizer)		8.0
90PC02 Black Pigment		1.1
		156.96

As used in the Polyair Foam Mixing Machine the above compound is split into 3 streams and supplied by 3 individual pumps.

"B" Component Hardener		"A" Component Prepolymer (10% NCO)		"C" Component Blowing Agent	
PTMG	40.2	PTMG	59.8	Nitrosan	3.9
1-4 BD	6.8	MDI	35.3	S-140	8.0
TMP	1.2		95.1		11.9
DC-193	0.64				
T-12	0.02				
90PC02	1.1				
	49.96				

This foam compound is run at a 102-isocyanate index based on the following equation:

$$\text{Isocyanate Index} = \frac{\text{No. of equivalents of MDI}}{\text{No. of equivalents of (PTMG, 1-4 BD, TMP)}}$$

In free-rise cup samples the cream time (time from discharge from mixer to initiation of blowing) is 3 to 4 seconds with a 22-to 24 second rise time (time from cream time to full expansion) and a 3 minute tack free time (time from foam pour until foam surface is not sticky to light touch).

The molded foam slab samples and boot uppers of the above formula were made using the Polyair LIM foam machine with a three-component head. The hardener and prepolymer were supplied at 220°F and the Nitrosan (in Santicizer 140) was supplied at 65°F. Cure time for molded foam boot upper parts was 18 minutes. This was with the upper rings at 170°F and a last temperature of 230°F.

The physical properties of the upper foam are as follows:

Density Lbs/cu. ft.	14.0
Compression Deflection @ 25%	
Room Temp. psi	8.2
-20°F psi	10.1
Compression Set @ 50% Defl.	
Room Temp. %	6.0
158°F %	78.9
Water Absorption %	
6" head - 48 hours	39.2
Gehman T10 °F	-81

H. Outsole Compound Evaluation

Some preliminary work had been done on the outsole formulation but as soon as the upper compound was finalized foam compound work was concentrated in this area. Outsoles were made using the same basic compound and mole ratios as were finalized in the upper compound. This was 1.0 PTMG (polytetramethylene ether glycol) 1.8 chain extender and 2.8 MDI (diphenylmethane diisocyanate). Outsoles were molded to the finalized boot upper using the Nitrosan blown upper compound but at a higher density of 24-26 pcf and with a

molecular weight per crosslink (M/C) of 16,500. Good appearing boots were made with this construction. The outsole felt flexible in the low temperature box at -20°F and had a good surface appearance as a result of the thin skin formed during molding. In order to get a quick indication of serviceability of this outsole, it was put on walk tests over some very severe terrain which included primarily sharp rocks. The boots were crossmated with boots made using Freon blown uppers and water blown outsoles made earlier on this contract. After a very few hours considerable chunking out and cutting was noticeable on the Nitrosan blown outsoles. Some cutting and minor chunking was evident on the water blown outsole but in general its condition was noticeably better. Additional walk tests under the same conditions confirmed the original results and indicated that the base compound must be altered.

At this point it appeared there were three basic approaches that could be taken:

1. Make a tougher, harder outsole using Nitrosan blowing agent by changing the mole ratios and increasing the chain extender.

2. Make a water blown outsole using the same basic ingredients and mole ratios as in the upper.

3. Adapt Uniroyal Civilian Boot Technology in making an outsole construction consisting of a solid urethane veneer (0.060") backed with a Nitrosan blown urethane foam.

It was decided to test compounds and constructions molded in the exact shape of the boot outsole. As a screening test for experimental outsole constructions the Naugatuck Footwear Outsole Flex Test was used. This test involves tying down the heel and toe of the outsole and flexing the outsole in approximately a 60° bend at the rate of 60 cycles/minute. An acceptable value is 200,000 cycles without failure.

The 1.0-1.8-2.8 Nitrosan blown outsole at 25 pcf did not flex well. Initial cracking started at 86,381 cycles and the outsole was badly cracked at 114,798 cycles. The tougher outsoles made by increasing the chain extender in ratios up to 1.0-3.0-4.0 felt stiffer in the cold box at

$-20^{o}F$, and based on previous experience it was felt the additional stiffness plus the added hardness would affect traction at low temperature to the point this would not be an acceptable approach.

It was decided to concentrate on the veneer and the water blown outsole approach. The veneer approach offers the advantage of a solid urethane layer with good abrasion resistance that can be backed up with a closed cell urethane foam for insulation. The water blown outsole is tougher by virtue of the urea linkages formed when the water reacts with the isocyanate to form CO_2 used as the blowing agent.

In order to evaluate the veneer approach, a silicone rubber mold backup plate was made that fit the existing outsole mold. The thickness of the veneer was approximately 0.060" except at the toe and heel extremes where it was increased to 0.160"-0.180". The veneer was a solid urethane piece and was molded on the LIM equipment. After the parts were molded they were placed in the outsole mold before shooting the backup foam that gives the desired outsole thickness and attaches the outsole composite to the upper. All veneer compounding also utilized the basic PTMG-chain extender-MDI polymer as used in the upper foam.

The first veneer evaluated was the base 1-1.8-2.8 mole ratio formula without the Nitrosan blowing agent (Shore A65). The foam backup was the same mole ratio blown with Nitrosan to a density of 20 pcf. The molecular weight per crosslink (M/C) was 16,500 in both formulations. This composite outsole was flexed on the Outsole Flexer. The part showed no flex crack at 255,335 cycles. At this point a 1/4" slit was put in the veneer in the ball area and flexing was continued. The slit grew to two-thirds the width of the outsole by the time 297,498 cycles had occurred.

To improve flex crack resistance and improve traction at low temperature the chain extender level of the veneer was reduced to 1-1-2. This gave a lower durometer veneer (Shore A-55-60) with a M/C of 17,000. The foam backup was kept at 1-1.8-2.8 and a 16,500 M/C. On the Outsole Flex Test this combination showed no cracking at 297,103 cycles. A slit was then made in the ball area and flexing continued. The slit grew to 60% of the outsole width in an additional 85,000 cycles. The crosslink density was then reduced to 170,000 M/C in the veneer and 71,600 M/C in the foam backup to make the composite more linear, and hopefully

more flex-crack resistant. Flexing was satisfactory to 244,012. After a slit was made, an additional 112,000 cycles were run, and at this time the slit had grown to 75% of the outsole width. Cut growth was still a problem.

A veneer going to the other extreme of being very hard was made. The mole ratio was 1-3-4 and gave a hard veneer (Shore A-75-80). The foam backup was 1-1.8-2.8 with an M/C of 71,600. This construction flexed 244,000 cycles with no failure and an additional 232,000 cycles after slitting with no cut growth. However, this was such a hard compound that based on previous experience the traction on snow and ice would not be satisfactory and it would be stiffer to the feel at these low temperatures. For these reasons no further work was done. At this point no satisfactory veneer composite was found for an outsole use.

Concurrently outsole compound work was also being done evaluating water blown outsoles. The basic PTMG-chain extender-MDI compound was carried over but water was substituted as the blowing agent instead of Nitrosan. With the modified compound and modified processing conditions the density was lowered without appreciably affecting the physical properties. Preliminary severe walk tests had indicated good resistance to chunking out. This toughness is attributed to the formation of urea linkages at the time of reaction of water with the MDI to release CO_2 gas. The outsole when exposed to -20°F is slightly stiffer but acceptable. Some shifting in water content and catalysis was necessary to process the foams, but good cell structure and density uniformity was accomplished. Outsoles made 22-25 pcf were submitted for flex test. A very slight crack appeared at the edge of the outsole at 228,657 cycles. At 262,204 the crack had grown only an additional 5%. To confirm the results of the Outsole Flex Tests, boots containing some of the same formulations were made up for walk testing. The boots were worn over a fixed course that included areas of black top (asphalt), crushed stone, and dirt with brush. Results of the walk tests basically substantiated the accelerated Outsole Flex Test. The Nitrosan blown outsoles chunked out and flex-cracked and were pulled out of test at 124 miles. The veneer-foam backed outsoles including the 1-1.8-2.8 and 1-1-2 veneers with the 16,500 M/C and 170,000 M/C Nitrosan blown foam backups showed some chunking out and flex cracking at 100 miles. The 1-1-2 veneer showed noticeable wear in the heel and toe areas at 100 miles.

The 1-1.8-2.8 veneer showed much less wear in these areas. The 1-3-4 veneer with the Nitrosan blown foam backup at 71,600 M/C wore very well and showed very little signs of wear at the heel and toe. There was also no chunking out or flex-cracking at 178 miles but the boot was withdrawn at this point to test the water blown construction since the traction would obviously be no good on snow and ice.

Water blown outsoles at 23-25 pcf showed up well in walk tests. There was some minor chunking out and some noticeable wear at the tip of the toe and butt of the heel at 430 miles. The areas of wear and degree of wear depended on the style of walking of the person testing the boot. The overall condition of the boots was good. At this point tests were stopped on these boots and additional pairs of boots with water blown outsole were initiated. At 462 miles the next water blown outsole looked very good. Other than a very small chunk out on one cleat, only the normal wearing away of extreme toe and heel areas was noticeable. Additional boots were walked and confirmed earlier results.

Boots with the finalized upper (1.0-1.8-2.8) and water blown outsoles, were submitted to the Project Officer for testing of insulation value. The insulation values obtained on the sectional copper foot were acceptable.

I. Finalized Outsole Foam Formulation, Processing Data and Physicals

Based on outsole flex tests, forced walk tests and flexibility as determined by feel at low temperature, the best overall construction was the water blown outsole. This was adopted as the standard outsole composition for the Arctic Boot. The mole ratio is 1.0-2.0-0.3(H_2O)-3.3.

The formula is as follows:

	Equivalents	Parts
PTMG (2000 MW)	0.1	100.0
1-4 Butanediol	0.2	9.0
Water	0.03	0.3
MDI	0.33	41.2
DC-193 (Silicone Surfactant)		0.21
DABCO WT (Catalyst)		0.05
90PC02 Black Pigment		1.12
T-12 (Catalyst)		0.005
		151.885

As used in the Polyair Foam Mixing Machine the above compound is split into two streams supplied by two individual gear pumps to the mixing head.

"B" Component (Hardener)		"A" Component (Prepolymer 15% NCO)	
PTMG	58.9	PTMG	40.2
1-4 BD	9.0	MDI	41.2
Water	0.3		81.4
DC-193	0.21		
DABCO WT	0.05		
90PC02 Pig.	1.12		
T-12	0.005		
	69.585		

This foam compound is run at a 99 isocyanate index. In a free blow cup sample the cream time is 3 to 4 seconds with a 32-to-40 second rise and a 34-to-36-second tack free time.

The individual molded water blown outsole samples for flex testing and the outsoles molded to the boot upper were made using the Polyair LIM foam machine. The hardener and prepolymer were supplied to the mixer at 165°F. The outsole mold outer rings were at 190°F and the sole plate was 170°F. This gives a cure time of 15-16 minutes.

The physical properties of the outsole foam are as follows:

Density Lbs/cu.ft.	24.39
Compression Deflection @ 25%	
Room Temp psi	49.9
-20°F psi	69.7

Compression Set @ 50% Defl.	
Room Temp. -%	9.4
158°F -%	72.3
Water Absorption	
48 hrs. - R.T. 6" Head	7.2
Hardness - Shore A	
Original	46
After 70 Hrs. @ 212°F	40
At -20°F	60
Gehman Test T-10	-76°F
Cut Growth 50,000 flexes	
Original %	0
After aging 70 hrs @ 212°F	0

V. OUTER SKIN EVALUATION

A. Evaluation of Fully Reacted Urethane Coatings

Evaluation work was done on urethane coatings for the outer skin of the boot. When it was felt the Freon blown boot upper was the direction that the final construction would take it was decided to work with fully reacted urethane polymers in a solvent blend. These coatings are available in a range of properties. Tensiles vary from 4000 to 10,000 psi and 100% modulus from 400 to well over 1500 psi. These type coatings lend themselves to a dip process since there is no pot life problem and that would be the simplest and least costly method of application. The assumption was made that with the 0.050"to 0.060" integral skin formed during the foaming of the upper, the urethane coating thickness would only have to be 0.010" to 0.015" to afford the proper degree of abrasion resistance and puncture resistance. The most promising initial coating evaluated was Daltoflex EP-1048. It was a fully reacted urethane in solvent (Toluene-Isopropyl alcohol) that gave films with 6000 psi tensiles, elongation of

680% and 100% modulus of 500 psi. The company making this product went out of the coating business and a new supplier had to be established. A number of coatings from various companies were obtained and evaluated. As a screening test for the coatings, modulus tests at $-20^{o}F$ were run. This test was run rather than the Gehman test because preparation of the good quality samples in the thickness required for the Gehman (0.080" to 0.085") was difficult. Thin gauge films could be used for modulus testing at $-20^{o}F$.

The most promising coatings were a series from Witco Chemical. Of this series the Y-304 was the lowest modulus coating and it was felt this was desirable for good flex life in this application. The Y-304 had a room temperature modulus at 100% of 975 psi which increased to 1500 psi at $-20^{o}F$. This was the lowest value of any of the initially received fully reacted urethane coatings. Work on applying the coating was initiated. Application by dipping was the proposed method. It was found adhesion of the dipped coating to the urethane foam upper was not adequate. It was possible to strip the coating from the foam with ease. The Y-304 coating had a base of a 50-50 blend of toluene-isopropanol. This blend did not attack the foam surface enough to give good adhesion of the film. It was found by adding DMF (dimethylformamide) for dilution of this coating from 25% to 12% solids for dipping resulted in a considerable improvement in coating adhesion. Further improvement was obtained by wiping the foam upper with either MEK (methyl ethyl ketone) or butyl cellusolve just prior to dipping. This removed any surface contaminants plus attacking the foam surface slightly. Using both these modifications, good adhesion of coating to upper foam was attained. It was found Witco had a coating (Y-343) basically the same chemically as Y-304 that was in a more active solvent blend (DMF, methyl cellusolve, isopropanol and toluene), so dipping efforts were switched to this coating. Dip coating solution was made up as follows:

	Parts/Weight
Witco Y-343 (35% TS)	100.0
DMF	133.0
E-2800 Black Pigment	3.0
OK 412 Flattening Agent	1.4

The dipping sequence was as follows:

1. Prewipe boot with damp solvent rag with either MEK or butyl cellusolve.

2. Allow surface to dry.

3. Immerse boot in dip solution - dwell 3 seconds.

4. Withdraw boot slowly letting coating drain evenly down sides of boot.

5. Remove excess coating off boot outsole.

6. Air dry 10-15 minutes at room temperature.

7. Oven dry at 150°F for 10 minutes.

8. Dip next coat following same procedure.

Multiple coats were applied to bring the coating to 0.010-0.015" thickness. Boots with this thickness coating were put out for walk tests. Flex cracks appeared in the vamp and back stay areas in approximately 100 miles.

The type flex in the vamp is by far the most severe in the boot upper. It was decided that future boots to be coated would incorporate a vamp patch. This involved taking a very thin piece of thermoplastic urethane sheet and adhering it only around the perimeter in the vamp area of the upper. This leaves a loose patch in the area of greatest stress. The boot is then dipped in the normal way but results in having the coating adhered to the patch but since the patch is not adhered in the center area, the upper foam and coating are not tied together and can flex individually.

Boots were coated substituting the Y-343 for the Y-304. The coated boot incorporated the vamp patch. This boot was walk tested and the results were better than any of the previous boots. There was no cracking in the vamp area and only minor cracks in other areas after 300 miles. However, Gehman Test data was received and indicated a T10 value of -11.5°F. Because of the marginal room temperature flex crack resistance and the poor Gehman value which indicates low temperature stiffness that would result in flex cracking at the expected service temperatures, it was decided to drop further evaluation of this type coating for the present.

In addition, it was becoming apparent that the Freon blown upper would not give the quality desired for the LIF-LIM boot. Work was already in progress on using Nitrosan as the blowing agent. With this compound no thick surface skin is formed so additional coating thickness would have to be applied to give adequate protection against abrasion and puncture. This eliminated dipping as a practical process since 8 to 10 coats were already being applied to attain a coating thickness of 0.010"-0.015".

B. <u>Evaluation of Two Component Reactive Urethant Coatings</u>

All coating development was switched to PTMG based coating systems. This polymer has good low temperature properties, good hydrolytic stability and moderate toughness. Several PTMG based coatings were tried and the ones that showed the most promise were Adiprene L-42 (DuPont) and Vibrathane (Uniroyal) B-602. These systems are two component systems that must be sprayed because of the limited pot life once the two components are mixed.

Films of coatings based on B-602 and L-42 were made up using both MDA (methylene dianaline) and mPDA (meta phenylene diamine) as curatives. Properties of these cast films are shown in Table 3. Results indicate these polymers are very similar in physical properties. Both these polymers are very similar in physical properties. Both these polymers passed the Gehman T10 low temperature test requirement of -65°F. Boots were made up and coated with these PTMG/MDI based coatings and put on walk test. The boots had a vamp patch incorporated. On these boots a wax (Staplers) was used to give release of the coating from the foam surface. The guiding criteria for the final choice of compound was processing and spraying of boots. In arriving at the final formulation for spraying a number of variations in solvent balance and curative level were tried in order to get the best combination of spray characteristics, flow, film smoothness and appearance. It was felt the B-602 using MDA as the curative and an isocyanate index of 103 gave a good overall balance of processing and film quality and this compound was used on the prototype boots and the 30 pair for Arctic Test. Wear test boots with this coating were walked 300 miles with no failure.

TABLE 3

COMPARATIVE PHYSICAL TEST DATA ADIPRENE L-42 AND VIBRATHANE B-602 FLIMS

Base	Curative	ISO Index	Tensile PSI	Modulus 100%	Modulus 300%	Elongation %	Tear PSI	Gehman T10-°F
B-602	mPDA	103	2932	515	808	700	330	**-84**
B-602	MDA	103	3350	421	763	447	310	**-74**
B-602	mPDA	110	2435	355	584	733	227	**-76**
B-602	MDA	110	2930	182	270	721	197	**-72**
L-42	mPDA	103	---	---	---	---	301	**-66**
L-42	MDA	103	3550	374	625	583	240	**-71**
L-42	mPDA	110	4066	426	730	600	249	**-74**
L-42	MDA	110	3260	215	441	633	199	**-67**

C. Finalized Outerskin Formulation, Processing Data and Physicals

The finalized formula for outerskin coating was as follows:

Component (A) Prepolymer		Component (B) Curative	
Vibrathane B-602	24.96 g	MDA	1.82 g
Toluene	24.96 g	THF	23.14 g
	49.92	MBK	24.96 g
		Black Pigment	0.08 g
		SF-69	0.08 g
			50.08

B-602 (PTMG prepolymer)

MDA (4.4' methylene dianaline)

THF (tetrahydrofuran)

MBK (methyl butyl ketone)

Black Pigment (Mircolith Black-CT)

SF-69 (silicone surfactant)

The ingredients are compounded as a (A) component (prepolymer) and a (B) component (curative). Both components contain a high percentage of solvent to facilitate spraying of the material onto the boot. A single-component air atomizing Binks spray gun (Model 62) with a pressure cup feed was used for spraying the boots. Since the spray gun handled only one compound, the (A) and (B) components were mixed together just prior to initiating spraying because the compounded material has only a nine-minute gel time. The pressure cup must be emptied before this time or plugging of the spray orifices results. It is proposed for production that two component electrostatic disc type spray equipment such as that offered by Ransburg Corporation, Indianapolis, Indiana be used. This equipment supplies the two reactive ingredients individually to a high speed rotating disc which mixes the materials, electrically charges the atomized particles, and

deposits them on the item to be coated in a short time span.

All boots for Arctic testing were hand sprayed and the coating was applied in three applications. A spray pattern was developed so that coating deposited on the boot varied from approximately 0.010" at the top to approximately 0.040" on the lower portion of the boot where the requirement for abrasion and puncture resistance is greatest.

The coating application procedure was as follows:

1. Weigh out and mix the masterbatches of the (A) and the (B) component.

2. Wipe the surface to be coated of one pair of boots with a damp MEK rag.

3. Apply a paste wax film (Stapler wax) in the area of maximum flex stress of the boots (area approximately 1.5" x 6" across the vamp above the toe area). Let dry 15 minutes at room temperature.

4. Mix the proper proportions of (A) and (B) components together to make a 400 gram batch and put in the pressure cup of the spray gun. Adjust air pressure to 25 lbs./in^2.

5. Spray first boot of pair while rotating boot and do not apply at too fast a rate or runs of liquid material will form. (Complete batch must be applied in approximately 7 minutes maximum to avoid gelling of compound in pressure cup.)

6. Allow boot to air dry for 10 minutes at R.T.

7. Mix second batch of compound as in #4.

8. Apply spray coat as in #5 to second boot of pair.

9. Allow boot to dry 10 minutes at R.T.

10. Repeat #4, #5 and #6 until three batches have been applied to each boot. (After the first coat the spray is concentrated primarily on the lower portion of the boot to build up the gauge in the area immediately above the outsole.

11. Let boots dry overnight at room temperature.

Using the above spraying sequence a coating weight of approximately 100 grams was applied to each boot. (size 10)

The physical properties of the sprayed film stripped off one of the boots supplied for the Arctic test were as follows:

Tensile - psi	4040
Elongation %	550
Tear psi	292
Gehman T10 (^{o}F)	-74

VI. SOCKLINING AND COLLAR

A. Constructions Evaluated

The socklining and collars used in making the prototypes and 30 pair of boots for test were fabricated from a urethane coated nylon tricot fabric. This coated fabric construction is presently being used in Uniroyal's commercial type insulated boot.

The socklining used in the previous contract (Contract DAAG17-72-C-0058) was a 2-ply fabric construction consisting of a nylon tricot/gum/cotton net fabric (SL-1). Towards the end of the previous contract, preliminary evaluation was done on newly submitted socklining constructions of urethane coated nylon tricot from Hygrade Shoe Findings Company (SL-2 and SL-3). Since there was not adequate time during the previous contract to evaluate this construction, it was decided to use the standard 2-ply fabric/gum construction. Subsequently a urethane coated nylon tricot was developed by Uniroyal, Inc. at its Mishawaka plant (SL-4). Preliminary evaluation of comparative physical properties is shown in Table 4.

There were several reasons for pursuing the use of the urethane coated nylon tricot (SL-4).

1. The weight of the sock (size 10) is approximately 25 grams as compared to 75 grams for the original SL-1 lining. This results in a weight reduction of 3.5 ounces per pair of boots.

TABLE 4

PHYSICAL PROPERTIES OF SOCKLINING

Physical Property	Test Method Fed. Std. No. 191	Sock Lining Spec.	SL-1 Uniroyal Nylon/ Cotton/ Rubber	SL-2 Hygrade #1 Nylon/ Urethane	SL-3 Hygrade Nylon/ Urethane	SL-4 Uniroyal Nylon/ Urethane
Adhesion, Lbs/2 in. (Wales direction)	Method 5950	2.0 Min.	2.0 Min.	2.0 Min.	2.0 Min.	2.0 Min.
Tear (Grams) (Wales direction)	Method 5132	2400 Min.	2633	765	2400+	2400+
Weight (oz./yd^2)	-	None	16.1	3.9	4.5	5.0
Gauge (In.)	-	None	0.037	0.012	-	Nylon tricot .010 Urethane .005 Overall .015
No. of Plies (Fabric)	-	None	2	1	1	1
Weight (Size 10) (Grams)	-	None	75	20	22	25
Count	Pick Last	None	-	-	-	Wales 54 Courses 62
Ball Burst Scott	-	-	-	-	-	180 lbs.
Elongation at 10 lbs.	-	-	-	-	-	Length 7.5% Width 22.5%
Ply Adhesion	-	-	-	-	-	Urethane to Nylon- Can't Strip

Uniroyal Laminate Composition - Nylon - Tricot Net #1826 (2.7 oz./sq. yd)
Gum - Natural Rubber
Cotton- 300 Cotton Net (3.6 oz./sq. yd)

2. The SL-4, because of its lighter weight, allows for better heat transfer from the boot last to the upper foam during foam molding and curing. This aids faster demold time.

3. The stretch of the SL-4 lining is greater than the SL-1 which makes the hooding of the last with the socklining easier during fabrication.

4. Market surveys on Uniroyal's insulated boot using the SL-4 type lining have indicated no problem in donning and doffing.

In earlier socklining studies the urethane coated nylon linings evidenced poor adhesion of the upper foam to the urethane coating and poor tear properties. These deficiencies were overcome by compound variations and improved coating techniques. Lining SL-4 showed excellent adhesion between the nylon fabric and urethane coating and also between this laminate and the upper foam. This construction performs two other functions in that the urethane coating also prevents strike-through of the foam into the fabric layer during molding of the boot and the nylon tricot serves as an extensible, abrasion resistant fabric lining that allows easy don and doff.

Before the completion of the current contract Uniroyal made the decision to discontinue producing the SL-4 item. A new supplier had to be established. Samples were obtained from outside sources. After several trial runs Reeves Bros., New York, NY, with guidance from Uniroyal developed a satisfactory socklining material as a replacement for the SL-4 construction. The code number assigned by Reeves is A 558 Revelle, Patent Black. The final prototypes and 30 pair of boots for test were made using this construction.

B. Physical Properties of the Finalized Socklining Construction

The physical properties of the finalized construction are as follows:

Tear (grams) wales direction		2640
Weight (oz/yd^2)		4.32
Gauge (in.)	*Nylon Tricot	0.010
	**Urethane	0.003

Count	Wales	40
	Courses	64
Ball Burst (lbs)		168
Elongation at 10 lbs.(%)	Length	25
	Width	40
Ply Adhesion		can't strip

* Nylon Tricot - 2.07 oz/yd^2, 2 Bar Jersey tricot net, heat set

** Urethane - PTMG polyether based polymer

This urethane coated fabric is purchased as roll goods in 54" width. From it is die cut the proper patterns for the sockclining and snow collar. Layouts of the parts are shown in Figure 17 and Figure 18. The socklining is cut as two pieces and then stitched together to form the sock. Black nylon thread using a zig-zag stitch is used to join the two parts.

This boot requires a snow collar. This part utilizes the same coated fabric construction as the socklining. The snow collar is die cut as a single piece. Eyelets are inserted and the part is seamed before it is final stitched to the boot upper during the finishing operation.

VII. PROCESS STEPS

The following outline covers the processing sequence required to produce a LIF boot, the prototype boots and 30 pair for the Alaskan test were produced following this procedure.

1. Prepare Collar (Reeves - A-558 Revelle - Patent Black)

Cut collar - clicker machine
Stencil collars
Eyelet collars
Seam collars
Deliver stitched collar to Boot Area

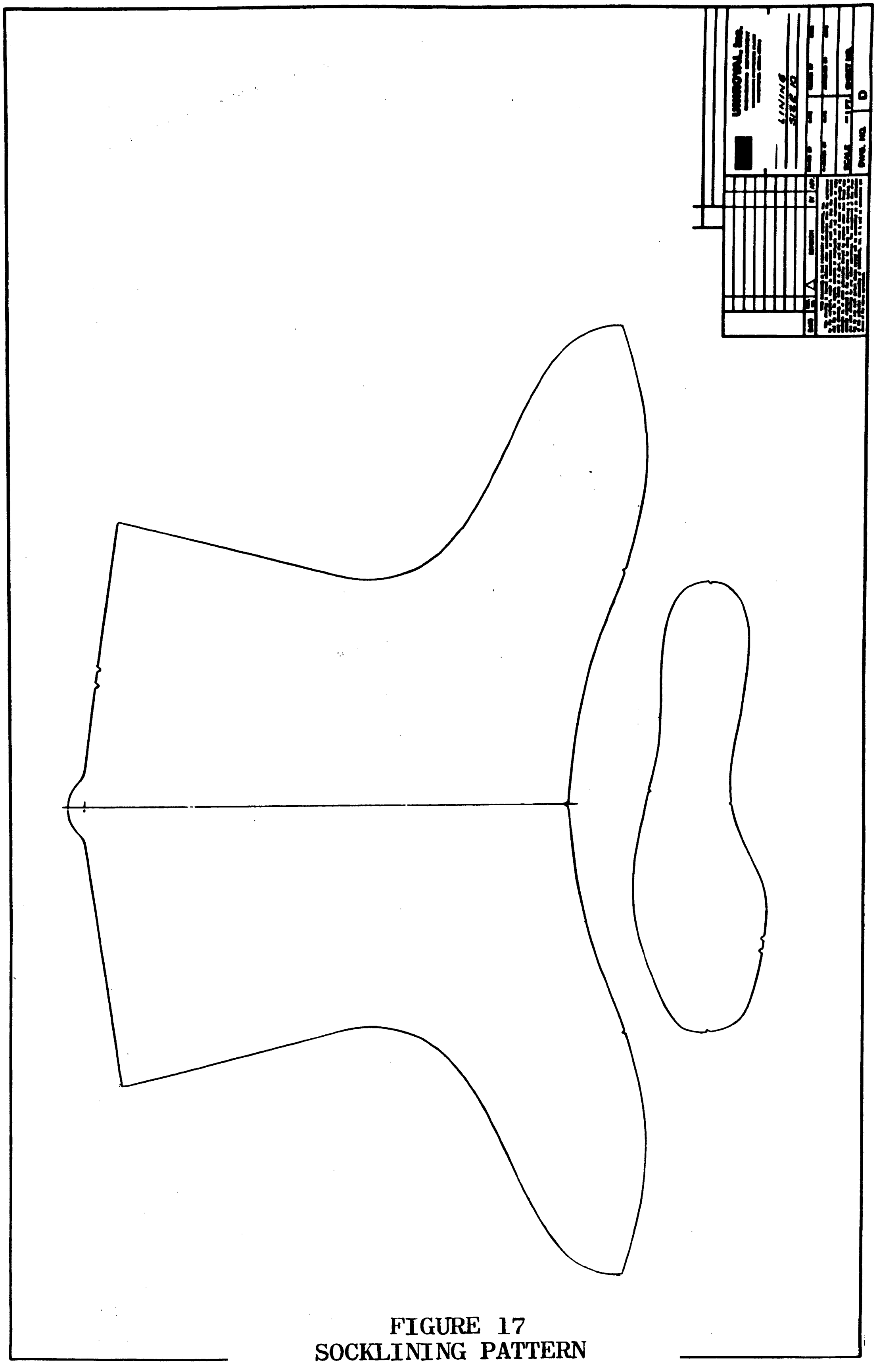


FIGURE 17
SOCKLINING PATTERN

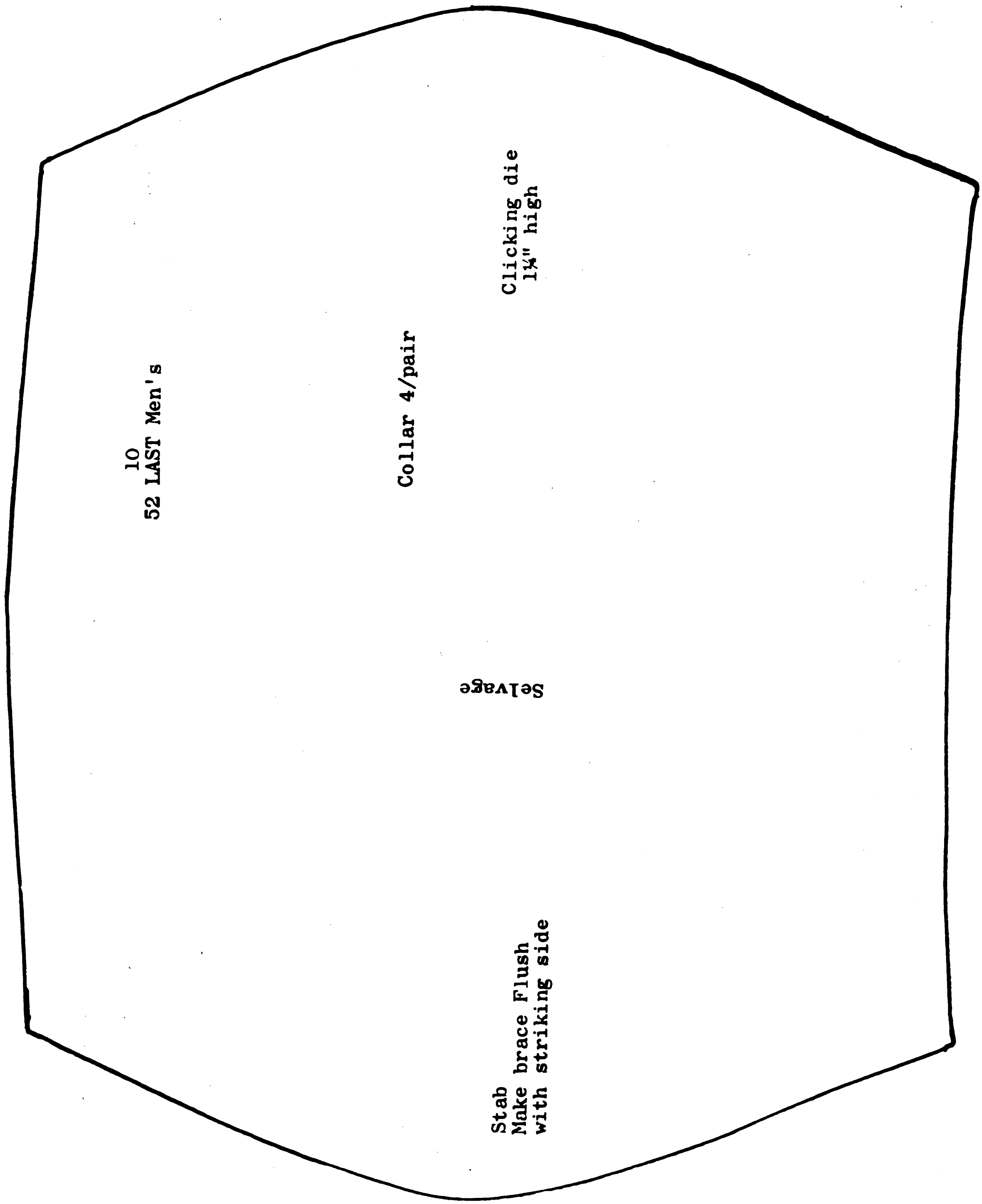


FIGURE 18
SNOW COLLAR PATTERN
(SIZE 10) FULL SCALE

2. <u>Prepare Sockling</u> (Reeves - A-558 - Patent Black)

Cut sockliner - leg liner
Stamp sockliner
Close stitch leg liner
Join sockliner
Deliver to Polyair LIM

3. <u>Mold Upper</u>

Heat PTMG and PTMG 10% NCO prepolymer in 140°F oven
Mix (B) component - PTMG, 1-4 BD, TMP, Silicone, Catalyst, Pigment (Add materials in listed sequence to 1 gallon container - stir 15 minutes)
Deliver (B) component to Polyair LIM--
(Transfer to supply pot set at 220°F)
Deliver (A) component (PTMG Prepolymer 10% NCO) to Polyair LIM (Transfer to supply pot set at 220°F)
Deliver (C) component (Refrigerated blowing agent at 50°F - Nitrosan in S-140) to Polyair LIM.
(Transfer to supply pot set at 65°F)
Clean mix head
Set ratio on Polyair LIM for (A) 100:(B)52.4; (C)12.5
Check ratio in cup shot - adjust if required
Check cup batch for cream, rise and tack free time
Hood sockliner on last
Wash socklining with Vythene (chlorinated solvent)
Apply tape to socklining seams (3M #29)
Position last in boot mold (set at 230°F)
Close upper rings (set at 170°F)
Close outsole rings (set at 165°F)
Inject Foam (55 impulses)
Cure foam (17 min.)
Open outsole rings
Retract last
Strip upper - remove flash

4. <u>Mold Outsole to Upper</u>

Heat PTMG and PTMG 15% NCO prepolymer in 140°F oven
Mix (B) component - PTMG, BD, water, catalyst, silicone pigment (Add materials in listed sequence to 1 gallon) container - mix 15 minutes)
Deliver (B) component to Polyair LIM
(Transfer to supply pot set at 165°F)
Deliver (A) component PTMG Prepolymer 15% NCO to Polyair LIM (Transfer to supply pot set at 165°F)
Clean mix head
Set ratio on Polyair LIM for 100(A)Component:85.4(B) Component

4. <u>Mold Outsole to Upper</u> (continued)

Check ratio in cup shot - adjust if required
Check cup batch for mix, cream, rise and tack free time
Heat preformed uppers (150°F - 10 minutes)
Slip upper on last
Position last in boot mold (set at 230°F)
Close upper rings (set at 170°F)
Close outsole rings (set at 190°F)
Inject foam (83 impulses)
Raise outsole plate (set at 170°F)
Cure outsole (15 minutes)
Open outsole rings
Open upper rings
Retract last
Strip boot

5. <u>Remove Flash, Inspect and Apply Outerskin</u>

Remove flash from boot outsole and upper
Buff outsole side wall and mold joint lines
Inspect
Repair if required
Set up spray booth
Warm, B-602 to 130°F
Mix (A) component (B-602-Toluene)
Mix (B) component (MDA, THF, MBK, SF69, Black Pigment)
Damp wipe boot with MEK
Apply vamp patch (Stapler Wax) - dry 15 minutes R.T.
Mix (A) and (B) components in 1:1 ratio
Stir and add to spray gun pressure can
Spray boot (while rotating by hand)
Dry boot (12 hours at room temperature)
Deliver to finishing area

6. <u>Trim, Collar, Final Inspect and Pack</u>

Trim boot to proper height
Stitch collar to boot
Pull out collar - insert lace
Stitch collar to outside of boot
Bar tack collar
Brand
Final inspect
Pack

VII. BOOT SPECIFICATIONS

The following data in Tables 5, 6, 7, and 8 compares the actual boot test data versus the tentative specifications as listed in the contract.

Table 5 lists boot dimensions of upper and outsole. Points 1 and 2 are slightly above spec. as a result of trials run to determine if relieving this area would aid in reducing air entrapment when evaluating the Freon blown compound. It was not needed for the Nitrosan blown compound. The only other discrepancy is point 18 which is slightly below gauge as a result of machining in the mold as received. This is a relatively small area and is not a drastic enough variation to affect serviceability of the boot.

A description of the points at which the thickness measurements of the upper were made are as follows:

a. Measurement points 1, 2, 3, 4, 5, and 6 are all located at the top edge of the boot. Points 1 and 2 are located on each side of the front mold parting line. Points 3 and 4 are located on each side of the rear mold parting line. Points 5 and 6 are located on each side midway between the front and rear mold parting line.

b. Measurement points 7, 8, 9, 10, 11 and 12 are exactly in the same position relative to the mold parting lines as those in the paragraph above except that they are all located on a line parallel to the top edge of the boot and 6 inches down from the top edge of the boot.

c. Measurement points 13 and 14 are located on each side of the rear mold parting line approximately 8-1/2 inches down from the top edge of the mold parting line.

d. Measurement points 15 and 16 are located 5 inches from the bottom of the outsole measured from the front of the toe along each side of the mold parting line.

e. Measurement points 17 and 18 are 2 inches above the bottom of the arch at the point where the sole lugging begins.

f. Measurement points 19 and 20 are located 3 inches from the bottom of the outsole measured from toe on each side of the front mold parting line.

g. Measurement points 21 and 22 are located 2 inches above the bottom of the outsole and 3-1/2 inches back from each side of the front mold parting line.

Table 6 lists physical test data for the outsole, upper and outer skin. The values established for the specification were tentative and subject to change. The compression deflection values are somewhat higher but do not detract from boot comfort or performance. The compression set will be slightly higher than the specification at elevated temperature since this is a closed cell foam and at this temperature and degree of compression, gas is forced out of the cell walls and results in lower recovery of height.

Table 7 lists physical test data for the socklining material. Table 8 itemizes the component weights of the complete boot and shows a total weight of less than 28 oz. per boot which meets the contract requirement.

Water pickup values obtained by immersing the entire boot (with snow collar removed) for 16 hours at room temperature was 1.2%. The maximum allowable water pickup is 5%.

TABLE 5

BOOT DIMENSIONS AT POINT LOCATIONS AS PER CONTRACT

Upper Section Point Location	Specification	Size 10 Right	Size 10 Left
1	0.100"-0.200"	*0.213"	0.140"
2	0.100"-0.200"	*0.213"	0.150"
3	0.100"-0.200"	0.175"	0.150"
4	0.100"-0.200"	0.175"	0.150"
5	0.100"-0.200"	0.155"	0.150"
6	0.100"-0.200"	0.173"	0.180"
7	0.500"-0.700"	0.602"	0.570"
8	0.500"-0.700"	0.600"	0.580"
9	0.500"-0.700"	0.515"	0.530"
10	0.500"-0.700"	0.535"	0.545"
11	0.400"-0.600"	0.530"	0.455"
12	0.400"-0.600"	0.550"	0.530"
13	0.500"-0.700"	0.660"	0.650"
14	0.500"-0.700"	0.660"	0.670"
15	0.600"-0.800"	0.710"	0.710"
16	0.600"-0.800"	0.705"	0.700"
17	0.700"-0.900"	0.710"	0.735"
18	0.700"-0.900"	0.650"	0.610"
19	0.700"-0.900"	0.710"	0.710"
20	0.700"-0.900"	0.700"	0.700"
21	no range given	0.740"	0.805"
22	no range given	0.705"	0.620"
Upper Size		Fits size 10 last	

* - Mold was relieved to determine effect on molding upper

Outsole Section Point Location	Specification	Right	Left
Heel(incl.cleat)	a 1.75"-1.85"	1.62"	1.58"
	b 1.75"-1.85"	1.63"	1.58"
Ball(incl.cleat)	a 1.00"-1.10"	1.30"	0.94"
	b 1.00"-1.10"	1.10"	1.05"
Arch	a 0.75"-0.85"	0.94"	0.94"
	b 0.75"-0.85"	0.95"	0.91"
Cleat	a 0.20"-0.30"	0.25"	0.25"
	b 0.20"-0.30"	0.25"	0.25"
Outsole Size		Fits size 10 upper	

TABLE VI

PHYSICAL PROPERTIES DATA OUTSOLE, UPPER AND OUTERSKIN

Physical Property	Test Method	Outsole Spec.	Outsole Actual	Upper Foam Spec.	Upper Foam Actual	Outerskin Spec.	Outerskin Actual
Color		Black					
Density lb/ft^3	ASTM D2406-65T Pars 62 thru 67	25 Min. 30 Max.	24.4	10 Min. 15 Max.	14.0		
Tensile Strength (PSI)	ASTM D412-66					2700 Min.	4040
Ultimate Elongation %	ASTM D412-66					500 Min.	550
Compression Deflection @ 25% at Room Temp. (PSI)	ASTM D1056-67T Pars 17 thru 20	35 Max.	49.9	6 Max.	8.2		
at -20°F (PSI)		+30% Max	69.7	+50% Max.	10.1		
Compression Set at 50% Deflection	ASTM D1056-67T Pars 21, 22 and 23						
at Room Temp, %		15 Max.	9.42	10 Max.	6.0		
at 158°F		60 Max.	72.27	70 Max.	78.9		
Cut growth 50,000 flexes original %	ASTM D1052-55	200	0%				
After aging 70 hours 212°F %	ASTM D573-67T	200	0%				
Gehman Test T10	ASTM D1053-65 (except Pars. 8 & 9)	-65°F	-76°F	-65°F	-81°F	-65°F	-74°F
Water Absorption % 6 inch head 48 hours	Fed. Std. 601 Method 1241	8 Max.	7.2	50 Max.	39.2		
Tear Resistance Die C (PPI)	ASTM D624-54					250	292
Hardness Shore A Original	ASTM D2240-64T	45 Min 65 Max	46				
After aging 70 hrs. at 212°F	ASTM D573-67T	$\pm$ 10	-6				
Hardness Change at -20°F		$\pm$15	+14				

TABLE 7

PHYSICAL PROPERTIES OF SOCKLINING AND SNOW COLLAR MATERIALS

Physical Property	Test Method Fed. St. No. 191		Values Spec.	Actual
Tear (Grams) (Wales Direction)	Method 5132		2400 Min.	2640
Weight (oz./yd^2)	Method 5041		6 Max	4.32
Gauge (In.)				
Nylon Tricot	Method 5030		0.010"	0.010"
Urethane			0.005"	0.003"
Count				
Wales			54	40
Courses			62	64
Ball Burst Scott (lbs.)	Method 5120		180	168
Elongation at 10 lbs. (%)		Length	7.5	25
		Width	22.5	40
Ply Adhesion	Method 5950		*C.S.	C.S.

* - Can't Strip

TABLE 8

BOOT WEIGHT DATA ON ARCTIC TEST BOOTS

	Right	Left
Size	10	10
Style	Collar	Collar
Type Sock	Urethane/Nylon	Urethane/Nylon
No. of Boots	30	30
Weight (Final) Grams (Av)	756	749
Weight of Collar Grams (Av)	12	12
Weight of Lace Grams (Av)	4	4
Weight of Coating Grams (Av)	99	97
Weight of Outsole Grams (Av)	323	318
Weight of Upper Grams (Av)	307	306
Weight of Socklining Grams (Av)	21	22

IX. CONSLUSIONS

1. Molds were designed and fabricated for making an Arctic Boot utilizing a method in which two separate compounds specifically formulated for the upper portion and outsole portion of the boot can be injected at two different times during a single molding cycle.

2. The mold carrier including the dual sole plate feature functioned well.

3. Liquid Injection Molding Equipment proved to be a satisfactory method of mixing and metering urethane foam compounds.

4. Liquid Injection Molding provided a good approach for the making of lightweight insulated footwear by a process that lends itself to automation.

5. Formulations developed produced good quality urethane foam boots.

6. Thirty pair of boots were produced and twenty-five pair were sent to Alaska for testing, while five pair were sent to NDC.

APPENDIX A

LIST OF MATERIALS

Material (Trade Name)	Chemical Name	Source
Adiprene L-42	Polyether, Urethane Prepolymer	E.I.DuPont DeNemours
Butanediol	1-4 Butanediol	GAF Corp.
Dabco	Triethylene Diamine	Air Products & Chemicals,Inc.
Dabco WT	Urethane Catalyst	" "
Daltoflex EP1048	Polyester Urethane in Solvent	ICI America
DC-193	Silicone Surfactant	Dow Corning
DMF	Dimethyl Foramide	Ashland Chem. Company
E-2800 Black	Black pigment in Epoxy Resin	Pigment Dispersions,Inc.
Freon 11B	Trichloro Mono Fluoro Methane	E.I.DuPont DeNemours
Freon 113	Trichloro Tri Fluoro Ethane	" "
MBK	Methyl Butyl Ketone	Eastman Chem. Products
MDA	Methylene Dianaline	Dow Chem.Co.
mPDA	Meta Phenylene Diamine	GAF Corp.
MDI	Di Phenyl Methane Diisocyanate	Mobay Chem. Co.
MEK	Methyl Ethyl Ketone	Celanese Chem. Co.
Methylene CL	Methylene Chloride	Dow Chem. Co.

APPENDIX A

LIST OF MATERIALS

(continued)

Material (Trade Name	Chemical Name	Source
Microlith Black CT	Black Pigment	Ciba' Geigy
Nitrosan	N,N'-Di Nitroso N,N' DiMethyl Terphthalamide	E.I.Dupont DeNemours
OK Flatening Agent		Degussa, Inc.
90PC02 Black Pigment	Black Pigment Paste	Harwick Chemical Company
Polymeg 2000 (PTMG)	Poly Tetra Methylene Ether Glycol	Quaker Chemical Company
SF-69	Silicone Surfactant	General Electric
Santicizer S-140	Cresyl Diphenyl Phosphate	Monsanto Chem. Company
SM Additive	Emulsifying agent - 50% water	Bayer AG
Stapler Wax	Mixture of Waxes	H. F. Staples & Company
T-9	Stannous Octoate	M&T Chem,Inc.
T-12	DiButyl Tin Dilaurate	" " "
Toluene	Toluene	American Cyanamid
THF	Tetra Hydrofuran	Quaker Chem.
3041 Black	Furnace Black in Plasticizer	Inmont Corp.
TMP	Tri Methylol Propane	Celanese Chem. Corp.

APPENDIX A

LIST OF MATERIALS
(continued)

Material (Trade Name)	Chemical Name	Source
UL-1, UL-2, UL-22	Modified tin catalysts	Argus Chemical Corp.
Vitrathane B-602	Polyether, Urethane prepolymer	Uniroyal Chem. Div.
Voranol CP 4701	Polyether Triol	Dow Chemical U.S.A.
Y-304, Y-343	Fully reacted polyester urethane in solvent blend	Witco Chemical Company
1829 Nylon Tricot Net	Two Bar Jersey Tricot Net - 2.07 oz/yd^2	Gehring Textile Company

APPENDIX B

EQUIPMENT SUPPLIERS

Equipment	Description	Source
Mold Carrier-1547 Mold	Desma Mold Station Desma Arctic Boot Molds	Compo Industries
LIM Machine	Foam Metering and Mixing Equipment	Polyair Maschinenbau